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## Preface

This Work Plan for "In Situ Chemical Remediation of Radionuclides in Soils" (also, formerly known as, "In Situ Dynamic Underground Stripping") describes activities to be conducted in support of Technical Task Plan No. RF121101. Tasks described in the Work Plan will be conducted jointly by a number of DOE sites including: Rocky Flats Plant, Los Alamos National Laboratory, and Lawrence Livermore National Laboratory.

The Work Plan format was taken from Section 3.5, "Preparing the Work Plan" in EPA's *Guide on Conducting Treatability Studies under CERCLA*, EPA/540/R-92/071a.

This work is being performed at Rocky Flats under Work Package 1432B.

## 1.0 Project Description

### 1.1 Introduction

Soils (and groundwater) contaminated with trace amounts of plutonium, americium, uranium mixed with volatile organic compounds (VOCs) and dense non-aqueous phase liquids (NAPLs) remain lingering problems in many remediation programs. Large volumes of contaminated soils may require processing to reduce contaminants to acceptable (yet undefined) levels.

At the Rocky Flats Plant (RFP) site, there are several below-ground locations that are contaminated with NAPLs/VOCs and radionuclides (plutonium, americium, uranium). The particular focus in this study is OU2/903 Pad area which contains radionuclides (plutonium, americium, and uranium), DNAPLs (VOCs: trichloroethylene (TCE), carbon tetrachloride (CCl<sub>4</sub>), tetrachloroethene (PCE), chloroform, methylene chloride; and NVOCS: cutting oils and lathe coolants). These contaminants sometimes occur in concentrated plumes, such as those of DNAPLs present at RFP's OU2/903 Pad in the clays and silt of Rocky Flats alluvium, and in pore spaces and fractures of sedimentary sandstones, siltstones, and claystones. The permeability of these geologic units may permit the percolation of these contaminant plumes and subsequent migration and eventual discharge of these contaminants as seeps into the surface waters. Mitigation and/or remediation of this non-radionuclide contaminant source are described in the OU2 Subsurface IM/IRA.

This proposed work constitutes Task 2 of the existing EM-50 funded TTP for Plutonium in Soils Integrated Demonstration Sampling Support. We will evaluate the use of thermally enhanced aqueous extraction processing of soils for the removal of radionuclides. The concept marries the technologies of redox, chelation, and steam processing to meet the challenge of RFP's OU2/903 Pad Area soils. The FY93 effort for this project will conduct proof-of-principle and bench-scale evaluations of chemically enhanced steam stripping for the mobilization and removal of radioactively-contaminated soils. The FY95 goal is to demonstrate an *in situ* soil extraction process which uses chemically enhanced steam injection to mobilize and remove radionuclides — especially, plutonium and americium — from contaminated RFP soil. This effort is part of the treatability studies for remedial screening and selection process for actinide contaminated soils in OU2's 903 Pad Area.

Testing will be conducted in three phases: (1) select promising chelator-redox systems using fast-turnaround, lab-scale, chemically enhanced steam extraction tests, (2) further reduce chemical enhancers to the more promising chelator-redox agent systems using bench-scale, soil-column washing tests, and (3) optimize perhaps the most promising chelator-redox systems using parametric bench-scale, soil-column washing tests. The objectives of this task will be:

- To select chelating/redox systems appropriate for OU2 soils, and define test matrix and test plan for laboratory studies and bench-scale tests.
- To perform lab-scale tests that evaluate plutonium and americium mobilization/removal efficiency resulting from chemically-enhanced steam.
- To perform bench-scale tests to evaluate mobilization of plutonium and americium using chelating agents under suitable redox conditions that simulate *in situ* conditions.

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## 1.2 Site History

Treatability studies will be performed on soils from the 903 Pad. The 903 Pad Area, encompassing the original 903 Drum Storage Site, was used from October 1958 to January 1967 for storage of radioactively contaminated oil drums whose contents were described by Calkins (1970).

"Most of the drums transferred to the field were nominal 55-gallon drums, but a significant number were 30-gallon drums. Not all were completely full. Approximately three-fourths of the drums were plutonium-contaminated, while most of the balance contained uranium. Of those containing plutonium, most were lathe coolant consisting of a straight-chain hydrocarbon mineral oil (Shell Vitrea) and carbon tetrachloride in varying proportions. Other liquids were involved, however, including hydraulic oils, vacuum pump oil, trichloroethylene, perchloroethylene, silicone oils, acetone still bottoms, etc...and in 1959 or possibly earlier ethanolamine was added to the oil to reduce the corrosion rate of the steel drums."

An estimated 5,000 gallons of liquid (Freiberg, 1970) containing 86 g (5.3 Ci) of plutonium leaked into the soil. Site grading in preparation for applying an asphalt cap over the area included moving "slightly" contaminated soil. A total of 33 drums of radioactively contaminated rocks were removed, and two courses of clean fill material were placed over the site. The asphalt covering was applied some two months later (Freiberg, 1970). The cover is approximately 8 centimeters (cm) thick and underlain by approximately 15 cm of loose gravel and 8 cm of fill dirt.

## 1.3 Project and Subtask Descriptions

The project will be conducted on 903 Pad area (sub)soils and in several phases comprising six subtasks. Strategic decision points, which allow judgment of the technology's promise and practice, are included in the project timeline.

### Subtask 1. Bench-Scale Work Plan

This task covers the preparation of this work plan for bench-scale testing which follows "Suggested Organization of Treatability Study Work Plan" in EPA's *Guide on Conducting Treatability Studies under CERCLA* (EPA/540/R-92/071a).

This task will also include completing, as required, operational safety analysis plan (OSA), job safety analysis (JSA) plan, health safety (H&S) plan, and standard operating procedures for the bench-scale tests for handling radioactivity and performing radioactive experiments prior to starting any bench-scale experiments at RFP.

### Subtask 2. Field Activities of the 903 Pad Area

This task will identify, based on past RFP OU2 work, and sample surface soils from locations which ensure sample representativeness. Soil will be collected and handled according to LANL or RFP procedures. The soil will be screened for radioactivity levels to ensure adherence to H&S radiological protection constraints before transferring to LANL/TA-48 or Bldg 881 for bench-scale tests.

### Subtask 3. Bench-Scale Testing

A majority of FY93 laboratory work will be performed at LANL to meet the accelerated schedule. Bench-scale testing will be a significant collaboration between RFP and LANL in FY94. FY94 treatability tasks will be coordinated and completed at both RFP and LANL in a joint effort. We will investigate the effectiveness of various redox and chelating agents that will mobilize plutonium and americium under steam conditions (near 100°C). Since plutonium solubility and chemistry varies with oxidation state, various reducing/oxidizing conditions will be evaluated for their impact on mobilizing plutonium. We will also investigate the stability of chelating agents under steam conditions.

A systematic study to establish optimum conditions with the various chelating agents is also crucial in deciding whether to proceed further for Subtasks 4 through 6. Because of the large number of tests involved, some tests will be performed at LANL some bench tests will be performed at RFP. The RFP radiochemistry lab in Bldg 881 will perform additional bench-scale experiments and support the pilot-scale testing program.

### Subtask 4. Conceptual Pilot-Scale Design (FY94)

This subtask will produce a conceptual pilot-scale design for the field operation. The design is anticipated to include chemically enhanced steam injection and associated feed and support subsystems, process control and monitoring technology, and any effluent collection and treatment subsystems. The steam injection system will take advantage of existing steam service or will include a boiler, piping, fuel, tanks, etc. Approximately 12 to 16 extraction/injection wells will be installed in the 903 Pad area.

### Subtask 5. Review and Analysis Assessment (FY94)

This subtask will conduct safety analyses and risk assessments, and evaluate safety design of equipment to be used in the conceptual design (Task 4) and field demonstration (Task 6). Plans and procedures for operations including S/O testing will be completed.

### Subtask 6. Pilot Test / Field Demonstration (FY95)

This task will conduct the actual field demonstration at the 903 Pad site.

## 2.0 Treatment Technology Description

### 2.1 Summary

There are various remediation approaches such as physical, chemical, biological, and thermal treatment, that can be used to remedy — whether by removal or stabilization — radionuclides and organics in soils and groundwater. Steam together with various types and concentrations of redox and chelating agents will be used to remove (i.e., mobilize and wash away) radionuclides contaminating selected RFP soils. Once radionuclides are mobilized, the radionuclide-rich (aqueous) mobile phase is driven by the steam front to extraction wells where it is collected and subsequently treated by more conventional wastewater technology. The approach uses a combination of steam injection/vacuum extraction and chemical action to mobilize radionuclides from soil where they can be subsequently treated by conventional technology.

## 2.2 Substrate/Soil Characterization

Retention of contaminants in a solid matrix (such as soils) varies with the physical and chemical properties of both the contaminant and the soil/solid phase. Contaminants are generally displaced by two mechanisms: (1) by physically, driving or flushing the contaminant from the substrate, (2) by chemically, dissolving contaminant and/or substrate to release the contaminant, or by some combination of (1) and (2). Detailed knowledge of substrate/soil properties, chemistry, and nature of the substrate-contaminant interaction is extremely useful in predicting washing behavior, designing lixiviation systems, and shortening the process development time. Substrate characteristics are also important to predicting its response to chemical treatment.

Some information on contaminant and soil physical and chemical properties, useful in designing a treatability study, is available. Although recent soil characterization information (important because of the earlier excavation activity at the site) is not available, Hicks and Blakeslee (1981) reported limited soil physics and chemistry for samples collected from the 903 Pad area. Activity versus particle-size fractionation gave the following:

Table 1. Dry Screened 903 Pad Soils\*

Fraction	> 4.0 mm	2.4 - 4.0 mm	0.42 - 2.4 mm	<0.42 mm
Weight %	60	4	12	24
Pu (dpm/g)	240	1400	3100	29000
Am (dpm/g)	150	270	560	4100

\*Soils dried at 100°C for 5 days. Data from Hicks and Blakeslee (1981).

Soil chemistries of selected, dried 903 Pad soils were also reported:

Table 2. Chemical Analysis of 903 Pad Soils\*\*

Element	Al	Ca	C	Fe	K	Si	Na
Sample 1	5.4	0.9	0.8	1.7	2.5	30	1
Sample 2	5.2	3.0	1.4	2.1	2.3	21.5	1

\*\* Data from Hicks and Blakeslee (1981).

This information should be used guardedly since recent studies suggest some mixing of the original and capping/fill materials has occurred. M. Z. Litaor (1993) of the RFP ER program is currently evaluating physical and chemical characteristics of 903 Pad soils; a report will be available by end FY93.

## 2.3 Soil Washing

EPA's Eagle et al. (1993) have demonstrated a soil washing plant for the treatment of radioactively contaminated soils at two Superfund sites. Soil washing operations were evaluated for their performance in reducing the volume of contaminated soils. Their program uses a four-tiered approach consisting of: (1) soil characterization, (2) bench-scale testing, (3) process development units, (4) pilot plant development where the results of each tier are used to decide whether to proceed to the next tier.



## 2.4 Soil Washing at RFP

Soil decontamination and washing evaluations have been conducted at RFP since the early 1970s and results have appeared in reports in the internal and external literature. R. L. Olsen et al. (1980) described the decontamination of the 903 Pad area following cleanup of the leaking drums in 1968. They reported that radiological contamination of 2000-300,000 dpm/100 cm<sup>2</sup> had penetrated the 903 Pad soils to a depth of 20 cm.

Hicks and Blakeslee (1981) summarized a decade of soil characterization and bench-scale attrition scrubbing studies performed at RFP on RFP 903 Pad Area soils. Plutonium in these soils occurs in both particulate (0.2-um mean diameter associated with soil particles) and dissolved (or perhaps colloidal) forms. Wet screening and radiometric characterization of the soils showed that a majority of plutonium (and americium) was associated with soils of the 2.4 mm and less size fraction. Attrition scrubbing of soils with hot (80°C) distilled water or aqueous solutions of: chemical agents (e.g., H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaClO, Na<sub>2</sub>SiO<sub>3</sub>), chelators (e.g., oxalic acid, citric acid), detergents (e.g., Oakite NST), and surfactants (e.g., sodium dioctyl sulfosuccinate) showed varying decontaminating effectivenesses. Oxalic acid (0.1M), sodium hexametaphosphate (10%), and 10% detergent solutions were among the more effective decontaminating systems for the 2.4-4.0 mm soil fraction, removing 95-98% of the Pu and Am. However, residual contamination levels still exceeded 60 dpm/g (27 pCi/g) following the scrubbing process.

Hicks and Blakeslee (1981) also reported soil washing tests on soils from five DOE sites including RFP. Three aqueous solutions: (1) an aqueous pH 12.5, (2) 2% HNO<sub>3</sub>, 0.2% HF, 2% pine oil, and 5% hexametaphosphate, (3) 2N HCl were evaluated for decontaminating RFP, Hanford, Mound, INEL, and LANL soils. Variability in the effectiveness of the three-phase scrubbing process was noted for soils from the different DOE sites. Effectiveness of the solutions also varied with the soil size fraction tested.

Pettis and Kallas (1988) conducted bench-scale testing and reported that simple, room-temperature wet screening of 903 Pad soils was effective at decontaminating the greater than 4 mm size fraction (approximately 60 wt% of the total) to <5 dpm/g (2.3 pCi/g) Pu and Am. The >2.4 mm size fraction (approximately 65 wt% of the total) was decontaminated to less than 12 dpm/g (5.5 pCi/g) Pu and 6 dpm/g (2.7 pCi/g) Am by wet attrition scrubbing. The remaining, <2.4 mm soil fraction was treated by attrition scrubbing, ultrasonic scrubbing, oxidation, calcination, desliming, flotation, and heavy-liquid density separation. Although somewhat guarded because of results for selected size fractions, they concluded that attrition or vibratory scrubbing, and either mineral jig or acid leaching of this fraction would be effective for a decontamination goal of <30 dpm/g (14 pCi/g).

## 2.5 Steam Stripping

Of the various remediation approaches noted above, under the thermal category of remediation technologies, one innovative technology is dynamic underground stripping (DUGS) — which is an adaptation of steam injection and electrical heating. Steam injection accelerates removal of the NAPL contaminants and is combined with vacuum extraction to perform accelerated removal of volatile contaminants such as underground hydrocarbon spills and electrical heating accelerates the process. Steam injection technology has been demonstrated by LLNL for remediating NAPLs and VOCs in subsurface soils and clay layers. Aines and Newmark (1992), and Buettner et al. (1992) (LLNL) have successfully tested this technology, in combination with electrical heating, on a bench scale and small field scale for the removal of NAPLs/VOCs in

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soils or clay layers at LLNL. EPA's Vendor Information Service for Innovative Treatment Technologies (VISITT) reports that steam stripping technology is being commercialized by Praxis Environmental Services (San Francisco, CA) (Stewart, 1992).

## 2.6 Redox Chemistry

Mobilization of contaminants can obtain as a result of physical or chemical action. Chemically induced mobilization occurs either by chemical action on the contaminant directly (e.g., plutonium) or its support substrate (i.e., soil). In the case of plutonium-contaminated soils, the mobilization of soil-bound species depends to a large extent on the physical and chemical properties of both the plutonium and the soil.

Plutonium generally exists in three oxidation states: III, IV, and VI, and in the natural environment, plutonium is normally found in either the IV state or, to a lesser extent, the VI state. The oxidation state of the plutonium is a determining factor in its solubility — III and VI states being more soluble than the IV state, whereas, americium normally occurs only in the III state. Redox (or chemical *reduction/oxidation*) behavior of plutonium features highly in its propensity for dissolution, and modification of its oxidation state is an important tool in changing solubility. Cleveland (1971) has described conditions for both reduction and oxidation of Pu(IV) using a variety of chemical reagents. We will evaluate simple reducing and oxidizing agents and conditions to accelerate dissolution/mobilization of the plutonium (see Sec 4.1.2).

## 2.7 Chelation Chemistry

Mobilization of metallic contaminants is greatly enhanced by formation of strong attachments with chemical binding agents via chelation. Chelation chemistry and chelators (or chelates) are often used in association with metals to accelerate dissolution, and/or stabilize/maintain solubility by diminishing the tendency to readsorb or precipitate. Once resuspended or dissolved, the soluble species (in this case radionuclide-chelator complexes) are stabilized by their association with the chelate, which in turn enhances their continued mobility. A variety of complexing or chelating agents, including EDTA, are commonly used for this purpose. Chelating agents can also enhance dissolution by tightly binding the radionuclide and preventing readsorption or precipitation. Chelating agents or chelators to be evaluated are discussed in Section 4.1.2.

## 2.8 Chemically Enhanced Steam Stripping

We propose to marry the technologies of steam injection, redox, and chelation for the leaching/washing of radionuclides from soils. Steam injection/extraction technology, enhanced by redox and chelation chemistry, will be used to mobilize and flush away radionuclides contaminating RFP soils. Conceptually, the process is very similar in design to steam injection systems involving injection and downgradient extraction wells, but with novel modifications to the injection system to provide chemical addition upstream of the soil washing regime.

The technology will be refined to minimize chemical injection with the goal of conducting *in situ* evaluation or *ex situ* treatment with the eventual return of the treated soils to the site. The benefits of this approach include: (1) reducing the volume of contaminated soils, (2) avoiding extremely harsh conditions therefore improving the potential for soil post-treatment soil viability and/or replacement, (3) possible tailoring to contaminant and soil conditions, and (4) combining with steam stripping of VOCs. The approach is also potentially applicable to *in situ* operations.

### 3.0 Test Objectives

Testing will be conducted in three phases: (1) select promising chelator-redox systems using fast-turnaround, lab-scale, chemically enhanced steam extraction tests, (2) further reduce chemical enhancers to 5-10 promising chelator-redox agent systems using bench-scale, soil-column washing tests, and (3) optimize perhaps three of the most promising chelator-redox systems using parametric bench-scale, soil-column washing tests. The objectives of this task will be:

- To characterize the physical and chemical conditions of soils that are contaminated with plutonium and americium. This includes clay mineralogy of *in situ* materials.
- To select/obtain plutonium-contaminated subsurface soils from the 903 Pad area for lab studies and bench-scale tests.
- To select chelating/redox systems appropriate for OU2 soils and define test matrix for lab studies and bench-scale tests.
- To perform lab-scale tests to evaluate plutonium and americium mobilization/removal efficiency caused by chemically-enhanced steam conditions.
- To perform bench-scale tests to evaluate mobilization of plutonium and americium using chelating agents under suitable redox conditions that simulate *in situ* conditions.

### 4.0 Experimental Design and Procedures

#### 4.1 Experimental Design

##### 4.1.1 Background

Leaching agents were selected based on experience with similar systems and previous experimental results obtained with plutonium-contaminated soil from the Nevada Test Site (NTS). These experiments included size fractionation of air-dried soil from the NTS, and subsequent alpha particle counting of the different soil fractions to rank the size fractions according to their activity. The results indicated that *most of the plutonium was associated with soil particles less than or equal to 53 microns (53um) in size*. Consequently, all the leaching experiments were performed with soil from the NTS with a particle size of less than or equal to 53 um in size.

The experimental parameters of the NTS soil leaching experiments were: soil to solution ratio was 1:8, the contact time between the solution and solid phase was 24 hours, the concentration of all solutions was 0.1 M, and the separation of phases was conducted by centrifugation. The initial Pu-239 concentration of the NTS soil was approximately 3000 dpm/g (1360 pCi/g) and all tests were conducted at 20°C. The results are given in Table 3.

Table 3. Results of Plutonium-Leaching Experiments from the NTS Soils

Extractant	% Removal	Starting pH	Equilibrium pH
EDTA / 3% H <sub>2</sub> O <sub>2</sub>	22	4.4	7.7
EDTA	21	4.5	5.6
EDTA / 1 eq NaOH	14	8.0	8.6
EDTA / 2 eq NaOH	9	11.0	10.9
EDTA / 3 eq NaOH	5	12.3	12.0
Citric Acid / 3% H <sub>2</sub> O <sub>2</sub>	40	1.9	3.7
Citric Acid / 1 eq HNO <sub>3</sub>	18	1.4	3.1
Citric Acid	16	2.2	3.8
Citric Acid / 1 eq NaOH	12	3.8	5.2
Citric Acid / 2 eq NaOH	10	5.1	8.2
Citric Acid / 3 eq NaOH	2	11.6	10.2
Citric Acid / 4 eq NaOH	0	12.3	12.3
Na <sub>2</sub> EGTA	13	7.4	6.3
Na <sub>2</sub> EGTA / 2 eq NaOH	45	12.0	11.5

The results in Table 3 indicate that simple complexants can desorb plutonium from plutonium-contaminated soils, and that the addition of oxidizing or reducing agents assists in the plutonium-leaching process. Based on the knowledge of the contamination process at the NTS, we expect that plutonium-leaching of the plutonium-contaminated RFP soil will be comparable to that of the NTS soil.

#### 4.1.2 903 Pad Soil Testing Design Basis

The test matrix given in Table 4 shows seven leaching experiments being performed by LANL at 20°C under another project entitled "Leachability of Pu from RFP Soils."

Table 4. Test Matrix for Plutonium-Leaching Experiments Using Standard Leaching Techniques

complexants (↓) redox agents (→)	water	NaOCl	NH <sub>2</sub> OH-HCl	Dithionite
water		X	X	
Citrate/Bicarbonate				X
EDTA	X			
HNO <sub>3</sub>	X			
NH <sub>4</sub> CO <sub>3</sub>	X			
Citric Acid	X			

Table 4 experiments will test simple complexants, standard leaching techniques, and redox behavior of the plutonium in RFP 903 Pad soil samples. Based on early results from similar experiments and knowledge of standard redox and solution behavior of plutonium (Cleveland, 1970), the leaching-test matrix shown in Table 5 was designed. Tests will be performed under steam conditions, about 80-90°C, on the RFP 903 Pad soil samples under the chemical conditions shown in Table 5. Other suitable chelating and redox agents may also be considered and tested under the steam conditions as the test results become available.

Table 5. Test Matrix for Plutonium-Leaching Experiments Using Combination of Complexants and Redox Agents\*

complexants (↓) redox agents (→)	water	NaOCl	H <sub>2</sub> O <sub>2</sub>	Ozone/c atalyst	Ascorbate	NaHSO <sub>3</sub> /H 2S
water					X	X
EDTA/Bicarbonate			X			
EGTA	X					
Carbonate/Bicarbonate	X	X	X	X	X	X

\* As test results become available, other chelating and reducing agents may be added to the test matrix, as appropriate.

#### 4.2 Test Plan

Our efforts will be devoted to three main areas: leaching experiments, laboratory-scale column experiments, and laboratory-scale optimization, described below.

##### 4.2.1 Batch Desorption Experiments

Leaching experiments involve taking soil from the Rocky Flats OU2, adding a solution containing a complexing agent, mixing the two phases, separating the phases, and determining the amount of plutonium in each phase. These leaching experiments will be conducted at 80°C using the experimental set-up depicted in Figure 1. This set up consists of equilibrating tubes containing the plutonium-contaminated soil and the leaching solution in a shaker surrounded by a metal enclosure that is kept at 80°C using a recirculating oil bath. The actual procedure to be utilized for desorbing plutonium from the Rocky Flats soil will be TWS-INC-DP-05, R2 "Sorption, Desorption Ratio Determinations of Geologic Materials by a Batch Method," and LANL-INC-DP-86, RO "Sorption and Desorption Determinations by a Batch Sample Technique for the Dynamic Transport Task." The determination of the amount of plutonium in each phase will be performed by alpha spectrometry following the procedures in LA-1721, 5th edition "Collected Radiochemical and Geochemical Procedures."

Each experiment will be performed in duplicate. Determination of plutonium concentration in each phase will be performed by difference (determining plutonium concentration in an aliquot of leachate alone and assuming that any difference remained in the solid phase). Mass balance will not be done in these set of experiments to maximize the number of chemical agents/conditions screened and to accelerate the schedule.

Table 5 (above) gives ten chemical complexant-redox systems ("X") to be evaluated at 80°C under this project, and at 20°C under a related project entitled, "Leachability of Pu from RFP Soils." The concentration of the complexants in the leaching solutions to be utilized will be approximately 0.1M. The concentration of the redox agents in the leaching solutions will be 30-50% of the complexant concentration. The soil-to-solution ratio will be 1:20, the contact time between the solution and solid phase will be approximately 24 hours, and separation of phases will be conducted by centrifugation.

#### 4.2.2 Bench-Scale Column Experiments

Based on results of the batch experiments (performed in Section 4.2.1), additional tests will be conducted using the more promising solutions which will be eluted at 80°C through a column containing RFP soils. The procedure to be utilized for the column experiments is given in LANL-INC-DP-15, R3, "Crushed Rock Column Studies." The column experiments will be performed in duplicate. The amount of plutonium leached from the RFP soil will be determined by alpha spectrometry following the procedures in LA-1721, 5th edition, "Collected Radiochemical and Geochemical Procedures." The columns to be used will contain at least 25 g of RFP soil. Ten to 20 column volumes will be eluted to determine the amount of plutonium leached from the soil. Experimental conditions will be designed, to the extent practicable, to simulate *in situ* conditions.

#### 4.2.3 Bench-Scale Optimization Studies

The optimal leaching solutions will be used to optimize the experimental parameters to be carried into the bench-scale chemical steam stripping experiments. The studies in the laboratory-scale optimization will consist of maximizing the amount of plutonium leached from the RFP soil while minimizing the chemical loading of the leaching solutions utilized. Only environmentally-sound leaching solutions will be utilized in this effort. A careful mass balance of the plutonium concentration in each phase will be performed in this effort. The plutonium concentration in each phase will be determined by alpha spectrometry following the procedures in LA-1721, 5th edition, "Collected Radiochemical and Geochemical Procedures."

The equipment configuration to be utilized is depicted in Figure 2. The reactors will have steam introduced along with the optimal leaching solution into a column containing approximately 200 g of plutonium-contaminated RFP soil. The column will have an approximate internal diameter of 2 inches and a height of 6 inches and will be made of an inert material, such as the commercial polymeric material, PEEK. Five of these reaction vessels will be constructed at LANL to sustain a maximum pressure of 100 psi.

### 5.0 Equipment and Materials

The desorption experiments require:

- Containers with leak-proof caps for sample containment
- A shaker kept at 80°C as depicted in Figure 1
- Ultra and super speed centrifuges to separate the solid and liquid phases after the leaching experiments are completed
- Calibrated balance
- Analytical pipettes
- Standardized counters to determine the amount of plutonium in each phase after leaching

The column experiments require:

- Syringe Pumps
- Calibrated balance
- Commercially available measuring tools (i.e., ruler)
- Luer fittings with frits, tubing
- Rheodyne injection valve
- Polyetheretherketone (PEEK) or teflon tubing
- Fraction collector
- Test tubes

- Standardized counters to determine the amount of plutonium in each phase after leaching

The optimization experiments require:

- A reactor as depicted in Figure 2 whose column is made out of PEEK
- Standardized counters to determine the amount of plutonium in each phase after leaching

## **6.0 Quality Assurance Addendum**

The work plan quality assurance addendum is in Appendix A.

## **7.0 Sampling and Analysis**

Soil and other environmental materials from the sampling area will be handled according to procedures in the "EMD Operating Procedures Manual" (5-21000-OPS-FO, Rev. 51, 7/26/93), and according to requirements of a process-specific Operational Safety Analysis for soil tests at RFP. All RFP soils handled by LANL will be stored and handled according to TWS-INC-DP-83, R1 "Storage and Handling of Solid Samples."

Representative sampling of bulk soils for radionuclide analyses is a difficult to achieve without some pre-treatment by physical methods. (It is extremely time consuming to dissolve the large soil fractions required to accurately assess the plutonium loading.) Reproducibility of analytical methods is also complicated by heterogeneities in the soil matrix. To minimize this experimental difficulty and maximize information specific to the chemical/steam conditions, we will dry and sieve the soils prior to the bench-scale experiments. Assuming, as with previous studies, that the plutonium is associated with a particular size fraction in the RFP soils, we will select a soil size fraction for bench-scale testing, which both optimizes experimental logistics and performance, while maintaining sampling and analytical reproducibility.

## **8.0 Data Management**

Data acquisition and management at RFP follow the general DOE Standard DOE-ER-STD-6001-92, "Implementation Guide for Quality Assurance Programs for Basic and Applied Research," Criteria 4 and 6. Data and other experimental information, which is collected by RFP for the test program in Section 4, will be recorded and managed in accordance with RFP EMD procedure for "Scientific Notebooks."

At LANL, the data from procedures in test plan (Section 4) will be entered and stored in electronic spreadsheets using Microsoft Excel. Hard copies of the spreadsheets which will include the data obtained and any procedural deviations will be signed by the technician performing the work and the principal investigator. Electronic copies of the spreadsheets will be stored on a hard disk drive, which is backed up on to an optical disk on a weekly basis. All the procedures delineated in Section 4 follow the quality assurance guidelines of NQA-1.

## **9.0 Data Analysis and Interpretation**

The results of the experiments in Section 4 will be analyzed following the guidelines given therein. Experiments will be performed (at least) in duplicate and simple statistical methods applied to screening and parametric data. Effectiveness of radionuclide removal will be assessed by alpha spectroscopy of the soil washing liquids and/or soils following treatment. Because of

K-16  
7/75

the relative facility with which solution samples may be reduced for radioassay, radiometric methods will be preferentially performed using washing solutions to establish efficiency; residual soil levels will be determined by difference. Radionuclide mass balance will be checked by occasional soil analyses in the bench-scale tests in Sections 4.2.1 and 4.2.2, and regularly in the parametric tests given in test plan Section 4.2.3.

Although Hayden et al. (1980) have provided some discussion, no soil decontamination or targets levels are available. The test plan evaluates various chemical systems with a goal of "the best that can be done." Further evaluation of soil washing solutions, not effectively mobilizing plutonium to produce low soil residuals will be discontinued. This approach will accelerate early screening and refinement of options prior to optimizing/parametric studies in Section 4.2.3. Overall performance of washing solutions/conditions will be ranked based upon: effectiveness, efficiency, robustness, as well as other criteria including cost and environmental acceptability.

## **10.0 Health and Safety**

All health and safety aspects of the work to be performed as specified in Section 4 will follow the requirements of either the site-specific Health and Safety Plan (HSP) for RFP as modified by facility-specific requirements of the testing laboratory, or the Health and Safety Standard Operating Procedures of the Isotope and Nuclear Chemistry (INC) Division at LANL. INC's Standard Operating Procedures include instructions for handling, storage, and disposal of radioactive and hazardous materials at Technical Area-48, building RC-1 of the Los Alamos National Laboratory, where the work will be performed.

## **11.0 Residuals Management**

Residuals and investigatory materials will be characterized by process knowledge or assay to establish handling requirements. Residuals will be managed at the investigator's facility. At RFP residuals are covered in "EMD Operating Procedures Manual" (5-21000-OPS-FO, Rev. 51, 7/26/93) or according to building-specific requirements for waste disposition. All studies will follow the RFP Waste Minimization Plan which places emphasis on not generating or minimizing the generation of low-level waste (LLW) and/or mixed wastes. The treatability goal will be to maximize leaching efficiency while using minimal chemical treatment.

## **12.0 Community Relations**

In accordance with the draft IAG, the Rocky Flats Plant developed a Community Relations Plan (CRP) to inform and actively involve the public in decision making regarding environmental restoration activities. The plan addresses the needs and concerns of the surrounding communities as identified through approximately 80 interviews with federal, state, and local elected officials; businesses; medical professionals; educational representatives; interest groups; media; and residents adjacent to the Plant.

Current community relations activities concerning environmental restoration include: participation by Plant representatives in informational workshops; meetings of the Rocky Flats Environmental Monitoring Council; briefings for citizens, businesses, and surrounding communities on environmental restoration and monitoring activities; and public comment meetings on various ER Program plans and actions.



In addition, a Speakers Bureau provides Plant speakers for presentations to civic groups and educational organizations, and a public tours program allows the public to visit the Rocky Flats Plant. The Plant also produces fact sheets and periodic updates on environmental restoration activities for public information and responds to numerous public inquiries concerning the Plant.

### 13.0 Reports

Monthly letter reports will be provided to the RFP Principal Investigator. Additional semi annual and annual summary reports will be provided within 61 days following the 6th, 12th, 18th, and 24th project months. Monthly letter/progress reports will provide: summary of significant results, projection of accomplishments for the next period, and a review of issues and problems affecting schedule.

### 14.0 Schedule

Activities described under this work plan cover a multi-year effort containing several decision points. If successfully shown at proof-of-principle and pilot-scale stages, field demonstration of this chemically enhanced steam technology is expected to occur in 3-5 years. Activities planned for the near-term treatability testing of this approach are:

#### Task/Milestone Summary: FY 93

#### Date Complete

- a. Complete work plan, including test plan
- b. Initiate bench-scale tests
- c. Issue letter report on the bench-scale tests

08-09-93

08-13-93

09-30-93

TASK/MILESTONE  
SUMMARY

MILESTONE EXPLANATION

SAME ON PAGES 13 & 14

#### Milestone Explanation:

- a. The test plan is contained within this work plan.
- b. Collection and delivery of RFP contaminated soil samples to LANL. This includes the selection, collection, and shipment to LANL of soil samples from the 903 Pad area.
- c. Letter Report- A letter report describing bench-scale results and interim conclusions will provide sufficient details and information to substantiate continuing this effort to the subsequent phases including a Pilot-Scale Evaluation of this technology in the field.

A detailed schedule for FY 93 and 94 activities is shown in Appendix F.

### 15.0 Management and Staffing

This project is a joint effort among collaborators from RFP, LANL, and LLNL. The RFP Principal Investigator and Rocky Flats Office Project Manager will be the point contacts for the effort. The management and reporting structure is given in Figure 3. The fiscal plan calls 3.0 FTEs in FY94 and FY95. This includes mostly principals with support staff to support analytical and more routine tasks. See Figure 3 for the organization chart for this project.

## 16.0 Budget

### Funding Schedule:

This Work Plan provides \$380K in FY93 for Subtasks 1, 2 and initiation of Subtask 3 (bench-scale tests). FY93 funding for limited lab testing will be provided by LANL under Uranium in Soils Integrated Demonstration. LLNL will be funded to provide FY93 peer review. Portions of Subtask 3 will be carried over to FY94. Subtasks 4, 5 and 6 will be conducted in FY94 and FY95.

### Budget Summary (Dollars in Thousands):

Sub Task	FY93	FY94
1. Design bench-scale tests (work plan)	\$70	-
2. Conduct field sampling activities of the 903 Pad	30	-
3. Perform Bench-Scale Tests*	280	350
TOTAL	\$380**	\$350**

\* Of the total \$50K will be used by RFP to purchase of bench-scale equipment that will probably be costed in early FY94.

\*\* Actual FY93 expenses as of June 30, 1993 were \$38K and commitment of a total of \$90K is expected by September 30, 1993. Remaining FY93 funding will be carried over to FY94.

### Task/Milestone Summary: FY93

#### Date Complete

- |   |          |
|---|----------|
| a. Complete work plan, including test plan      | 08-09-93 |
| b. Initiate bench-scale tests                   | 08-13-93 |
| c. Issue letter report on the bench-scale tests | 09-30-93 |

### Milestone Explanation:

- The test plan is contained within this work plan.
- Collection and delivery of RFP contaminated soil samples to LANL. This includes the selection, collection, and shipment to LANL of soil samples from the 903 Pad area.
- Letter Report- A letter report describing bench-scale results and interim conclusions will provide sufficient details and information to substantiate continuing this effort to the subsequent phases including a Pilot-Scale Evaluation of this technology in the field.

### Technical Progress/Milestone:

#### FY 93

1. Prepare Bench-Scale Work Plan. This will be completed in early 8/93.
2. Deliver soil samples to LANL. This will be completed by the middle of 8/93.
3. Issue letter report on the bench scale test progress. This will be completed by 9/30/93.

Funding Basis:

	<u>FY93 (\$K)</u>	<u>FY94 (\$K)</u>
FTE	1.0	3.0
Labor	330	325
CE	50*	-
Subcontract	<u>0</u>	<u>25</u>
Total	\$380**	**

- \* The \$50K capital funding in FY93 will be used to purchase bench-scale equipment for the 881 Lab experiments and will be deferred to FY94.
- \*\* This is new activity involving support from LANL, LLNL, and RFP and is expected to have a FY93 carryover; funding level for FY94 is expected to require an additional \$350K.

## 17.0 References

- R. D. Aines, R. L. Newmark, "Rapid Removal of Underground Hydrocarbon Spills," *Energy & Technology Review*, UCRL-52000-92-7 (July 1992), p.1-7.
- H. M. Buettner, W. D. Daily, A. L. Ramirez, "Enhancing Cyclic Steam Injection and Vapor Extraction of Volatile Organic Compounds in Soils with Electrical Heating," UCRL-ID-109424, Lawrence Livermore National Laboratory, Livermore, CA, March 30, 1992.
- K. W. Calkins, Memorandum to L. M. Joshel, Dow Chemical Company, Rocky Flats Division, August 19, 1970.
- J. M. Cleveland, "The Chemistry of Plutonium," Gordon and Breach Science Publishers, New York, 1970.
- M. C. Eagle, W. S. Richardson, S. S. Hay, C. Cox, "Soil Washing for Volume Reduction of Radioactively Contaminated Soils," *Remediation*, Summer 1993, p. 327-344.
- K. J. Freiberg, Memorandum to E. A. Putzier, Dow Chemical Company, Rocky Flats Division, April 14, 1970.
- J. A. Hayden, D. W. Rutherford, K. Y. Gallagher, P. M. Arnold, J. R. Stevens, "Soil Decontamination Criteria Report, November 1980," RFP-3162, Rockwell International, Rocky Flats Plant, Golden, CO, December 10, 1980.
- J. E. Hicks, J. J. Blakeslee, "Soil Decontamination Process Development Closeout Report," AR 05-15-20-1 AL, Rockwell International, Rocky Flats Plant, Golden, CO, September 1981.
- M. Z. Litaor, personnel communication, July 26, 1993. Soil work in support of OU2 activities is currently under evaluation with a report due by end FY93.
- R. L. Olsen, J. A. Hayden, C. E. Alford, R. L. Kochen, J. R. Stevens, "Soil Decontamination at Rocky Flats," *Decontamination and Decommissioning of Nuclear Facilities*, M. M. Osterhout, Ed., Plenum Publishing Corp., 1980, p. 161-172.
- S. A. Pettis, A. J. Kallas, "Summary of Previous Soil Decontamination Studies Performed at Rocky Flats Plant," PSD88-0027, Rockwell International, Rocky Flats Plant, Golden, CO, June 1988.
- L. D. Stewart, K. S. Udell, "Thermally Enhanced Recovery In Situ," Praxis Environmental Services (San Francisco, CA), from EPA's Vendor Information System for Innovative Treatment Technologies (VISITT) database, Version 2.0.

## 17.0 Figures

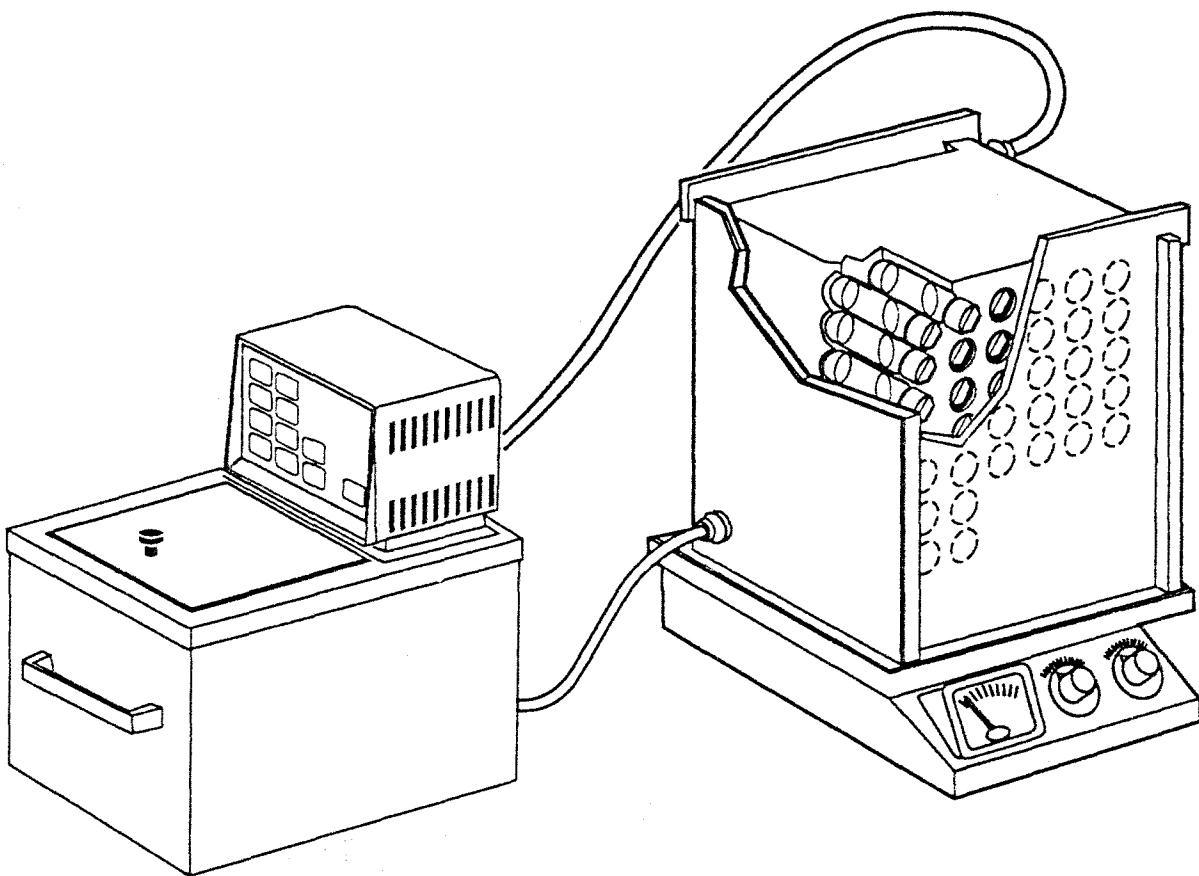
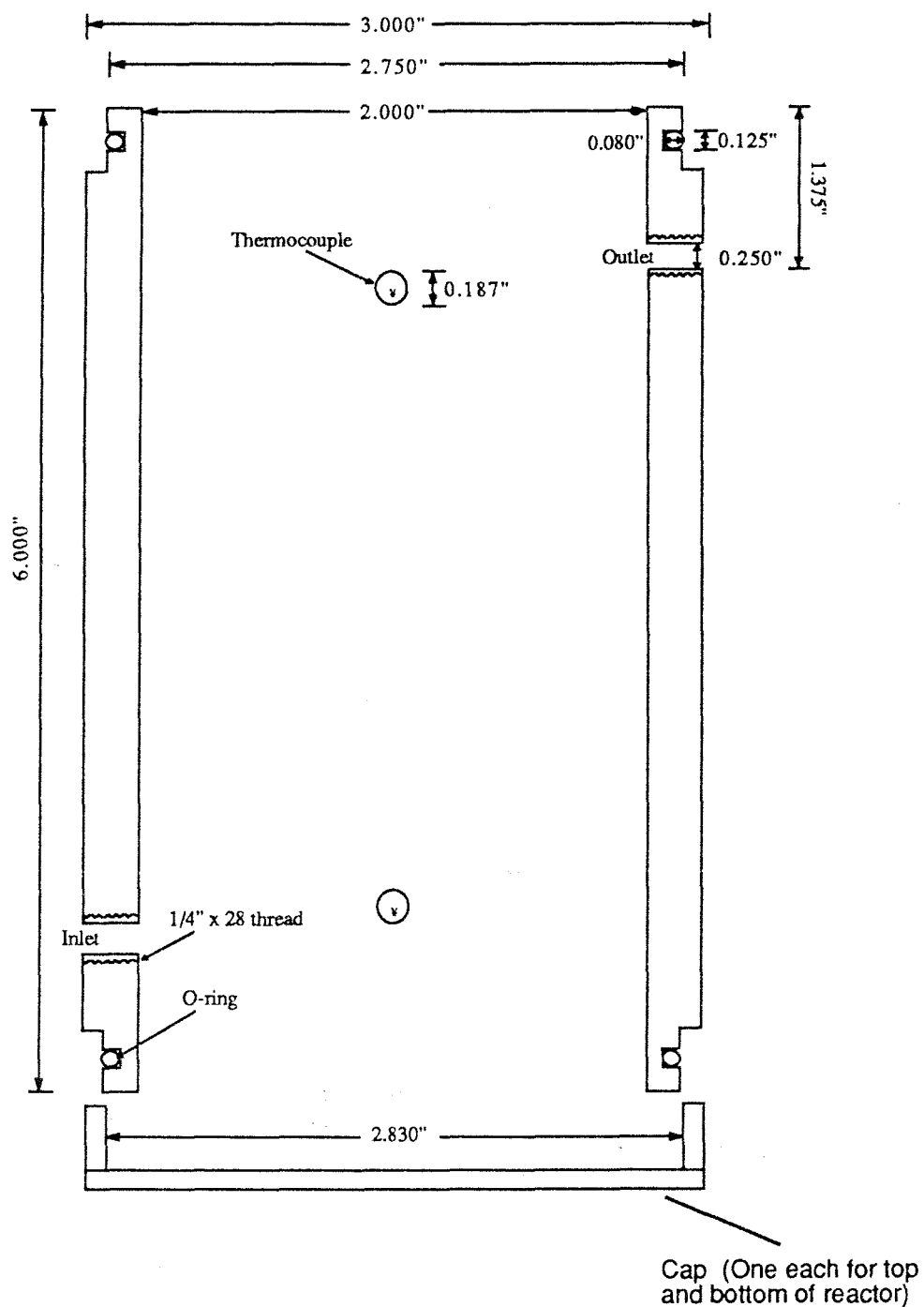


Figure 1. Equipment for Batch Desorption Experiments at 80°C.



(Not To Scale)

Figure 2. Bench-Scale Reactor for Plutonium Steam Stripping.

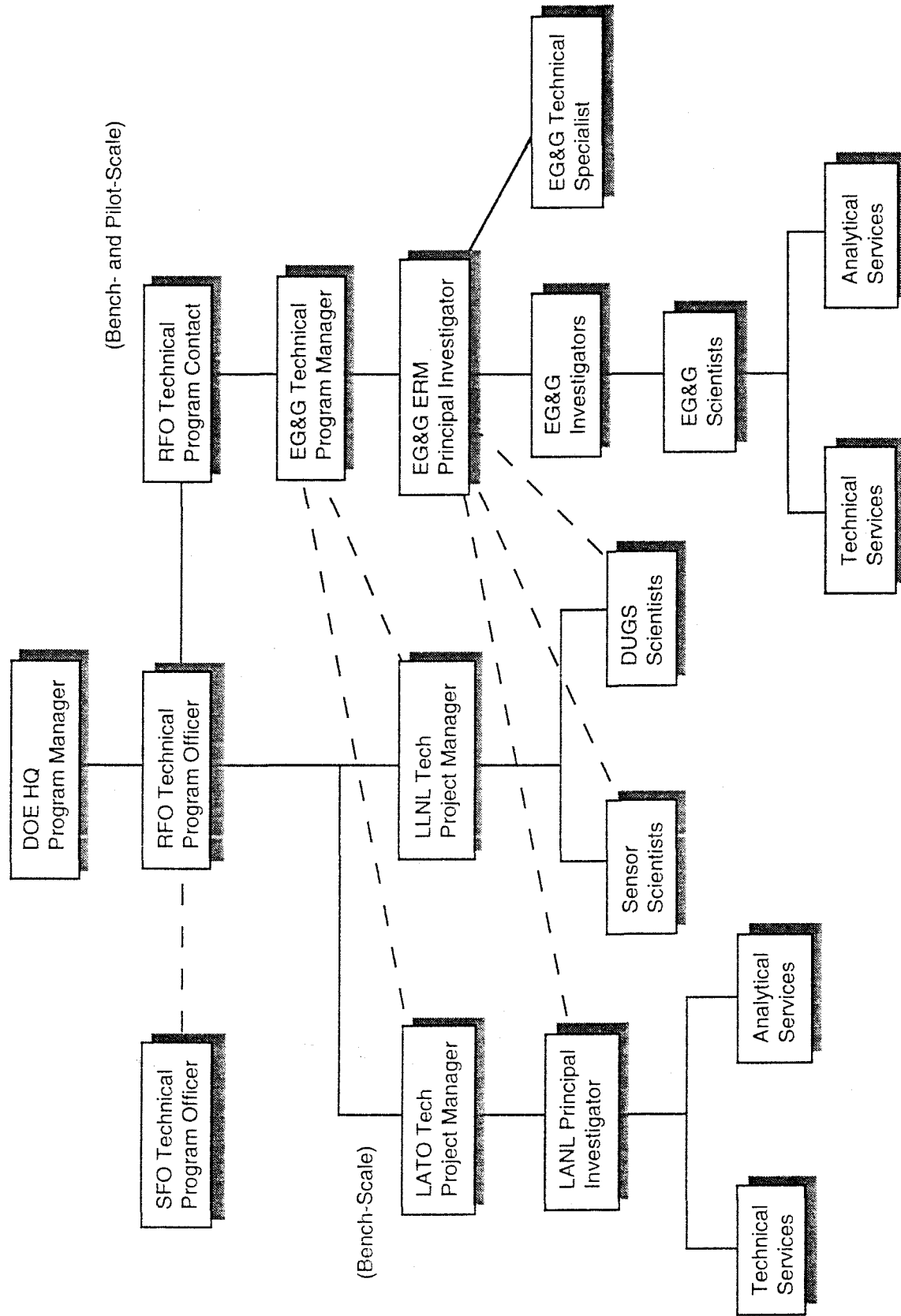


Figure 3. Management and Reporting Structure for In Situ Remediation of Radionuclides in Soils Program

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# APPENDIX A

## QUALITY ASSURANCE ADDENDUM



## Quality Assurance Addendum

### *Work Plan Quality Assurance*

Experimental work and tests described in this work plan is largely investigatory in nature with the goal of evaluating various approaches for chemically enhancing steam for the mobilization of radionuclides (metals). Testing is performed by trained, experienced investigators or their designee(s) following standard laboratory practices or procedures. Work will be conducted according to: (1) established or approved laboratory procedures when these are appropriate or available and/or (2) standard laboratory and investigatory practices, such as that covered the draft procedure *Use of Controlled Scientific Notebooks* (3-21000-ADM Procedure No. 5.10, Rev 0, draft F), and be based on standard literature methods and/or standard scientific practices.

Approved laboratory or investigatory procedures, or documented modifications thereof, are referenced in the work plan where available. All deviations from established procedures will be documented in laboratory or scientific notebooks and approved by the principal investigator. Work plan efforts will follow standard NQA-1, Level 3 laboratory and data management practices. As methods and practices become routine or standardized, procedures will be developed and approved for this work.

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# APPENDIX B

## ENVIRONMENTAL MANAGEMENT

### STANDARD OPERATIONS PROCEDURE

This is a  
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EG&G - ROCKY FLATS PLANT  
ENVIRONMENTAL MANAGEMENT

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**ROCKY FLATS PLANT**

**EMD OPERATING  
PROCEDURES MANUAL**

Manual No.: 5-21000-OPS-FO  
New Manual No.: 4-11000-ER-OPS-FO  
Procedure No.: Table of Contents, Rev 51  
Page: 1 of 4  
Effective Date: 07/26/93  
Organization: Environmental Management

**THIS IS ONE VOLUME OF A SIX VOLUME SET WHICH INCLUDES:**

VOLUME I: FIELD OPERATIONS (FO)  
VOLUME II: GROUNDWATER (GW)  
VOLUME III: GEOTECHNICAL (GT)  
VOLUME IV: SURFACE WATER (SW)  
VOLUME V: ECOLOGY (EE)  
VOLUME VI: AIR (AP)

**TABLE OF CONTENTS  
FOR VOLUME I: FIELD OPERATIONS**

<u>Procedure No.</u>	<u>Title</u>	<u>Rev. No.</u>	<u>Effective Date</u>
FO.01	Air Monitoring and Dust Control	2	05/12/92
FO.02	Transmittal of Field QA Records	3	05/22/92
DCN 93.01	Working Base Maps	3	05/12/93
FO.03	General Equipment Decontamination	2	05/12/92
DCN 92.01	EXPIRED (Clarification of Decontamination)	2	Expired
DCN 92.02	Update to Clarification of Decontamination	2	12/12/92
DCN 93.01	CPT Rods	2	02/16/93
FO.04	Heavy Equipment Decontamination	2	05/12/92
DCN 92.01	Expired	1	Expired
DCN 92.02	Expired	1	Expired
DCN 92.03	Consistency Change	1	09/18/92
DCN 92.04	Update to Clarification of Decontamination	2	12/17/92
FO.05	Handling of Purge and Development Water	2	05/12/92

DOCUMENT CLASSIFICATION REVIEW WAIVER  
PER R.B. HOFFMAN, CLASSIFICATION OFFICE  
JUNE 11, 1991

**ROCKY FLATS PLANT**  
**EMD OPERATING**  
**PROCEDURES MANUAL**

Manual No.: 5-21000-OPS-FO  
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FO.06	Handling of Personal Protective Equipment	2	05/12/92
DCN 92.01	Monitoring Change	2	09/18/92
DCN 93.01	Plastic Bagging Modification	2	02/17/93
FO.07	Handling of Decontamination Water and Wash Water	2	05/12/92
DCN 92.01	Consistency Change	2	09/18/92
FO.08	Handling of Drilling Fluids and Cuttings	2	05/12/92
DCN 92.04	EXPIRED (Clarification of Drill Cuttings)	2	Expired
DCN 92.05	EXPIRED (Handling of Drilling Fluids and Cuttings)	2	Expired
DCN 92.06	Clarification of Responsibility	2	09/09/92
DCN 92.07	Elimination of Drilling Requirements on Earthen Dams	2	09/10/92
DCN 92.08	Consistency Change	2	09/18/92
DCN 92.09	Clarification of Augering Technique for OU-6	2	10/28/92
DCN 92.10	Improve Tracking of Samples	2	12/07/92
DCN 93.01	Better Consistency of Drum Handling	2	06/29/93
FO.09	Handling of Residual Samples	2	05/12/92
FO.10	Receiving, Labeling, and Handling Environmental Materials Containers	2	05/12/92
DCN 92.03	EXPIRED (Replaced by DCN 93.01 dated 2/10/93)	2	Expired
DCN 92.04	EXPIRED (Decrease in Weekly Inspections of Gray Drums)	3	Expired
DCN 92.05	Requirement Reduction	2	09/16/92
DCN 92.06	Improve Accountability	2	10/15/92
DCN 92.07	Expired	2	Expired
DCN 92.08	Drum Log F or M Change	2	12/03/92
DCN 93.01	Clarification on Drums (REPLACES DCN 92.03)	2	02/10/93
DCN 93.02	Renewal (DCN 92.07)	2	03/17/93
DCN 93.03	Number of Drums per Pallet	2	05/11/93
DCN 93.04	Sample to Drum Traceability	2	06/23/93
DCN 93.05	Drum Labeling Change	2	06/29/93
DCN 93.06	Drum Sample Numbers	2	06/29/93

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ROCKY FLATS PLANT	Manual No.:	5-21000-OPS-FO
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<u>Procedure No.</u>	<u>Title</u>	<u>Rev. No.</u>	<u>Effective Date</u>
FO.11	Field Communications	2	05/12/92
FO.12	Decontamination Facility Operations	2	05/12/92
DCN 93.01	Tank Inspection Log	2	04/13/93
FO.13	Containerization, Preserving, Handling and Shipping of Soil and Water Samples	2	05/12/92
DCN 92.01	Chain of Custody	2	07/27/92
DCN 92.02	Improve Tracking of Samples	2	12/08/92
DCN 93.01	Chain of Custody Record	2	02/10/93
DCN 93.02	Air Bill COC	2	05/18/93
FO.14	Field Data Management	2	05/12/92
DCN 92.01	EXPIRED (Update Bottle Codes and Lab Codes to Current Status)	2	Expired
DCN 92.02	Clarification of Biological Locations (07/08/92- Extended)	2	11/20/92
DCN 92.03	Changes in Procedures (07/08/92 - Extended)	2	11/20/92
DCN 92.04	Expired	2	Expired
DCN 92.05	Update QA/QC Code List	2	09/28/92
DCN 92.06	Clarify Description	2	09/28/92
DCN 92.07	Update Bottle Code List	2	09/28/92
DCN 92.08	Add Sub-Contractor Abbreviations	2	10/14/92
DCN 92.09	Major Form Revision	2	11/03/92
DCN 92.10	Elimination of Non-Required Section	2	11/10/92
DCN 92.11	Update Bottle Code & Lab Codes to Current Status	2	12/09/92
DCN 93.01	New Codes	2	01/15/93
DCN 93.02	New Samplers and New Media	2	01/15/93
DCN 93.03	Field Data for RFEDS	2	02/10/93
DCN 93.04	RFEDS Back-up	2	03/18/93
FO.15	Photoionization Detectors (PIDs) and Flame Ionization Detectors (FIDs)	2	05/12/92

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ROCKY FLATS PLANT	Manual No.:	5-21000-OPS-FO
EMD OPERATING	New Manual No.:	4-11000-ER-OPS-FO
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	Organization:	Environmental Management

<u>Procedure No.</u>	<u>Title</u>	<u>Rev. No.</u>	<u>Effective Date</u>
FO.16	Field Radiological Measurements	2	05/12/92
DCN 92.04	EXPIRED (Seismic Lines)	1	Expired
DCN 92.05	Addition of HPGe	2	11/24/92
DCN 93.01	FIDLER Surveys	2	01/15/93
DCN 93.02	LUDLUM/FIDLER Guidance	2	06/29/93
FO.17	Determining Out-Of-Specification Analytical Results for Environmental Samples		To Be Added
FO.18	Environmental Sample Radioactivity Content Screening	1	05/12/92
DCN 93.01	Clarification of Procedure	1	01/11/93
FO.19	Base Laboratory Work	2	05/12/92
•FO.27	4-BO1-ER-OPS-FO.27 Collection of Floor/Equipment Hot Water Rinsate Samples	0	07/26/93

This is a RED Stamp

ROCKY FLATS PLANT  
EMD OPERATING  
PROCEDURES MANUAL

Manual No.: 5-21000-OPS-SW  
Procedure No.: Table of Contents, Rev 11  
Page: 1 of 2  
Effective Date: 07/23/93  
Organization: Environmental Management

THIS IS ONE VOLUME OF A SIX VOLUME SET WHICH INCLUDES:

VOLUME I: FIELD OPERATIONS (FO)  
VOLUME II: GROUNDWATER (GW)  
VOLUME III: GEOTECHNICAL (GT)  
VOLUME IV: SURFACE WATER (SW)  
VOLUME V: ECOLOGY (EE)  
VOLUME VI: AIR (AP)

TABLE OF CONTENTS  
FOR VOLUME IV: SURFACE WATER

Procedure No.	Title	Rev. No.	Effective Date
SW.01	Surface Water Data Collection Activities	2	05/12/92
DCN 92.01	Assure Quality Control	2	07/21/92
SW.02	Field Measurement of Surface Water Field Parameters	2	05/12/92
• DCN 92.01	<del>Allow Change in Instrumentation</del>	2	EXPIRED
• DCN 92.02	<del>Reduction in Chlorine Testing Requirements</del>	2	EXPIRED
DCN 93.01	Alkalinity Titration Delays	2	05/11/93
SW.03	Surface Water Sampling	2	05/12/92
SW.04	Discharge Measurement	2	05/12/92
SW.05	Base Laboratory Work		To Be Added
SW.06	Sediment Sampling	2	05/12/92
• DCN 92.01	<del>Reduction in Personal Protection Level Due to Local Knowledge</del>	2	EXPIRED
DCN 92.02	Clarification of Sampling	2	09/29/92
SW.07	Collection of Tap Water Samples	2	05/12/92

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**ROCKY FLATS PLANT  
EMD OPERATING  
PROCEDURES MANUAL**

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<u>Proc. No.</u>	<u>Title</u>	<u>Rev. No.</u>	<u>Effective Date</u>
SW.08	Pond Sampling	2	05/12/92
DCN 92.01	Clarification of Sampling	2	10/05/92
SW.09	Industrial Effluent and Pond Discharge Sampling	2	05/12/92
SW.10	Event-Related Surface Water Sampling	1	02/20/92
DCN 93.01	Table Replacement-Attachment 1	1	01/15/93
SW.11	Operation and Maintenance of Stream-Gaging and Sampling Stations	1	02/20/92
SW.12	Site Description	2	05/12/92
•DCN 92.01	<del>Reduction in Unrequired Quality Check</del>	2	EXPIRED
SW.13	Bacteriological Water Sampling	2	05/12/92
SW.14	Automatic Sampling		To Be Added
SW.15	River and Ditch Sampling	2	05/12/92
SW.16	Sampling of Incidental Waters	2	05/12/92
SW.17	Pond and Reservoir Bottom Sediment Sampling	0	09/25/92
DCN 93.01	Decontamination	0	01/15/93
SW.28	Field Locating Effluent Pathways and Drains	0	09/25/92
SW.29	Dye Testing Building Drains	0	09/29/92
SW.30	Field Locating Chemicals of Concern	0	09/25/92
SW.33	Dye Testing Foundation Footing Drains	0	09/29/92



## APPENDIX C

# SORPTION, DESORPTION RATIO DETERMINATIONS OF GEOLOGIC MATERIALS BY A BATCH METHOD

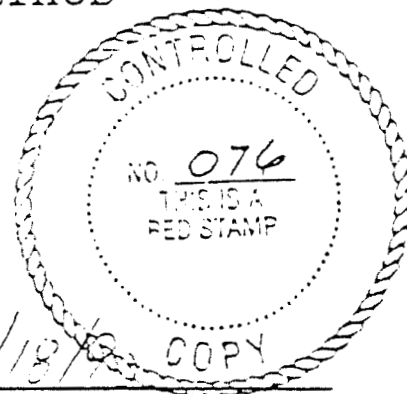
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TWS-INC-DP-05. R2

SORPTION, DESORPTION RATIO DETERMINATIONS OF  
GEOLOGIC MATERIALS BY A BATCH METHOD

Effective Date: July 23, 1990



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TECHNICAL PROJECT OFFICER, R. Herbst

7/9/90  
DATE

## SORPTION, DESORPTION RATIO DETERMINATIONS OF GEOLOGIC MATERIALS BY A BATCH METHOD

### 1. PROCEDURE IDENTIFIER: TWS-INC-DP-05

### INTRODUCTION

### 2. PURPOSE

The purpose of this procedure is to delineate the method for determining batch sorption and desorption coefficients for the distribution of various chemical species between geologic materials and natural or synthetic waters.

### 3. SCOPE

This document describes the procedure to be used for batch sorption and desorption experiments in the sorption task of the LANL YMP.

### 4. APPLICABLE DOCUMENTS

4.1 TWS-QAS-QP-05.2 "Preparation of a Detailed Technical Procedure"

4.2 TWS-QAS-QP-03.2 "Procedure for Preparation and Technical and Policy Review of Technical Information Products"

4.3 TWS-QAS-QP-12.1 "Procedure for Control of Measuring and Test Equipment"

4.4 TWS-INC-DP-35, "pH Measurements"

4.5 TWS-INC-DP-62, "Bulk NTS Well Water Samples"

4.6 TWS-INC-DP-63, "Preparation of NTS Core Samples for Crushed Rock Experiments"

4.7 TWS-QAS-QP-03.5 "Procedure for Documenting Scientific Investigations"

## 5. RESPONSIBILITIES

The PI has the responsibility for all operations. He/she may assign appropriate tasks to personnel trained to this DP. It is the responsibility of the users of this DP to adhere to the procedure. Investigators may direct deviations from the procedure upon approval of the responsible PI. It is the responsibility of the user to document such deviations in accordance with TWS-QAS-QP-03.5. If change requests are in process it is the responsibility of the user to document the procedure change in his laboratory notebook. It is the responsibility of the users of this DP to report unplanned deviations from this procedure to the responsible PI.

## 6. PRINCIPLE

This is a procedure for the determination of a batch sorption coefficient in which distribution of a single element or group of elements is measured between a sample of granulated (i.e., crushed) rock or mineral and an aqueous solution. In the procedure, a granular rock or mineral sample is first contacted with an aliquot of the ground water to be used in the sorption experiment. This step is intended to allow any new surfaces produced in the sample crushing procedure to react with the ambient ground water before contact with a particular radionuclide. The sample is then contacted with an aliquot of the chosen water composition spiked with the element(s) (i.e., radionuclides) of interest. The concentration(s) of the element(s) of interest in the water must be below the solubility of the least soluble compound of the element of interest that could form in the solution. After an appropriate reaction time, the water is separated from the solid phase and the concentration of the element(s) of interest are determined in the water and the solid. The ratio of the concentrations is obtained and called the sorption ratio. If the time over which the solid and water were contacted was equal to or exceeded the time required to reach a steady state sorption ratio, the ratio is called a sorption coefficient for the chosen element(s) in the particular water/solid system. The time required to reach steady state must be independently determined in time series experiments involving each of the rock and mineral types and each of the important radionuclides.

## 7. DEFINITIONS

7.1 The measured sorption or desorption ratio,  $R_d$ , is defined as

$$R_d = \frac{\text{amount or activity of the sorbing or desorbing species per g of solid}}{\text{amount or activity of the sorbing or desorbing species per ml of solution}}$$

7.2 tracer solution = original solution containing element(s) (i.e., radionuclides) whose sorption behavior is to be studied. Generally obtained from manufacturer or other LANL source.

7.3 stock solution = ground water solution containing the element(s) (i.e., radionuclides) whose sorption behavior is to be studied.

7.4 Ultra speed centrifuge = centrifuge capable of achieving a maximum speed of at least 65,000 rpm.

7.5 Super speed centrifuge = centrifuge capable of achieving a maximum speed of at least 20,000 rpm.

7.6 Ultra filter = filter with pore sizes less than 0.1 micron

## PROCEDURE

### 8. ADEQUATE AND APPROPRIATE EQUIPMENT, INSTRUMENTATION, AND SOFTWARE

Containers with leak-proof caps are required for sample containment. A shaker is used to equilibrate samples. Ultra and super speed centrifuges and/or ultra-filters are utilized to separate the solid and liquid phases after equilibration. Centrifuge rotors must be capable of withstanding the forces used for centrifugation. Calibrated balances must be used for determining weights in this detailed procedure. Analytical pipets must be used to measure volume quantities in this procedure. Standardized counters are used to allow accurate determination of radioactivities.

### 9. EXPERIMENTAL PREPARATORY STEPS AND VERIFICATION

9.1 Obtain a chemical analysis, including pH, Eh, major elements and trace elements, of the water to be used in the experiment(s). A recent water analysis and the unique identifier for the water sample used should be available as a result of the implementation of procedure TWS-INC-DP-62. If a recent water analysis is not available, transfer to a cleaned bottle a sufficient volume of water from the source volume (e.g., barrel) to carry out the planned experiment(s). Remove an aliquot from this bottle for the analysis of major and trace components.

- 9.2 Clean the labware to be used for the experiment. This is usually done by rinsing the labware with distilled water three times and drying in a clean area. Deviations or extensions from this cleaning procedure will be documented in the laboratory notebook.
- 9.3 In a cleaned bottle of sufficient volume, prepare the stock solution to be used in the experiment(s) by adding an appropriate amount of tracer solution containing each radionuclide of interest to the ground water to be used in the experiment. Because the tracer solution may have a pH that is different from the ground water, check the pH of the stock solution after addition of the tracer. Use procedure TWS-INC-DP-35. If the pH is different from that desired, add sufficient HCl or NaOH to the solution to achieve the desired pH. Agitate the bottle containing the stock solution on a shaker table overnight. Filter the stock solution through an ultrafilter with a 0.002 micron pore size or smaller (e.g., Millipore CX-30).
- 9.4 Determine the concentration(s) of the tracer element(s) in the stock solution. If the tracer element is present only in radioactive form, the concentration can be obtained by counting methods. If both radioactive and non-radioactive forms of the tracer element are present, additional methods of analysis will be required.
- 9.5 Determine the pH of the stock solution according to procedure TWS-INC-DP-35.
- 9.6 Determine the Eh of the final stock solution.
- 9.7 Determine the extent to which the elements of interest adhere to the walls of the container to be used in the experiment(s). This is done by transferring a known volume of the stock solution to each of the container types to be tested. After shaking the solution in the containers for at least 3 weeks, remove an aliquot of solution from the container and measure the concentration of the element of interest. If this concentration is less than the original concentration of the element in the stock solution, calculate the amount lost to the container per ml of solution. For the batch experiments, use the container type that shows the least loss to the container walls.
- 9.8 If a rock sample is to be used in the batch experiments, precondition the sample by placing an appropriate amount of the washed granular sample, obtained thru TWS-INC-DP-63, in a cleaned container with an aliquot of ground water to be used in the sorption experiment. Usually, the ratio of water to rock/mineral is 20ml to 1g.

If a different ratio is used record the details in the notebook. Shake the water/rock mixture for at least 3 weeks. Separate the water from the rock/mineral sample, filter it thru an 0.002 micron filter (e.g., Millipore CX-30), and have the filtrate analyzed for the items given in 9.1. Wash the solid sample as described in TWS-ENC-DP-63, take an aliquot, and have it analyzed for major and trace elements, and mineralogy.

#### Notebook Entries

Verify that the following entries are made in the laboratory notebook before starting the experiment:

- 9.1.1 Major and trace element composition, pH and Eh, of the water to be used in the experiment(s) and associated analytical errors.
- 9.1.2 Method of cleaning labware if different from the one specified in item 9.2.
- 9.1.3 pH of stock solution after final preparation.
- 9.1.4 Eh of the final stock solution and the method of measurement.
- 9.1.5 Concentration of tracer element(s) in the stock solution and associated analytical errors. Verify that this concentration is below the saturation level of the least soluble compound of the element(s) of interest that could form in this solution. Also describe the method of preparation of the stock solution if different from that given in 9.3 (i.e., the experimental steps used for preparation, notebook TWS number and pages used specifying these steps, or a detailed procedure number).
- 9.1.6 Container type to be used in the experiment(s) and the percent of element(s) of interest lost to walls of this type of container.
- 9.1.7 Record the water/rock ratio used if different than 20:1.
- 9.1.8 Composition of the water and the mineralogy of the rock/mineral sample resulting from the preconditioning step 9.8.

#### 10. SUITABLE AND CONTROLLED ENVIRONMENTAL CONDITIONS

No special conditions are required for this DP. If any special conditions are utilized (e.g., controlled atmosphere), record them in the laboratory notebook.

## 11. EXPERIMENTAL STEPS AND ACCEPTANCE OR REJECTION CRITERIA OF DATA COLLECTED

### 11.A. Sorption Procedure

- 11.A.1 Transfer an aliquot (by weight or volume) of stock solution to a cleaned and dried container of the type specified in 9.7.
- 11.A.2 For a batch experiment involving granulated rock, weigh out into a small evaporating dish between 50 and 100 mg of moist pre-equilibrated crushed rock prepared in step 9.8. Dry the sample at 105 degrees C overnight. Weigh the dried sample and subtract the result from the initial weight.
- 11.A.3 Weigh a cleaned and dried container of the type specified in 9.7.
- 11.A.4 For a batch experiment involving granulated rock, add a sufficient amount of moist pre-equilibrated granulated rock to the container weighed in 11.A.3 to obtain the desired weight of dried rock in the container given the water content of the moist granulated rock obtained in 11.A.2. Weigh the container with the granulated rock. For an experiment involving a pure mineral separate, simply weigh out a sufficient amount of the dry mineral into the container weighed in 11.A.3. If the mineral sample is not dry, follow the same procedure as described for moist granulated rock.
- 11.A.5 Add a known volume or weight of the stock solution to the container and record Julian date. Weigh the container with the mixture.
- 11.A.6 Mix the containers in 11.A.1 and 11.A.5 using an end-over-end laboratory mixer. Mix at a speed between 0.1-0.5 RPM. Usually, the container(s) is mixed for three weeks. Record the mixing time in the laboratory notebook.
- 11.A.7 After the shaking is complete, weigh the container(s).
- 11.A.8 For an initial separation of phases, centrifuge the containers for one hour at a minimum of 5,000 rpm. After centrifugation, remove most of the supernatant



from each container and transfer to a clean container. Take an appropriate sized aliquot of this solution and determine its pH following TWS-INC-DP-35.

- 11.A.9 If the concentration of the element(s) of interest in the solid is required or if a desorption experiment is planned for the solid sample, remove as much of the remaining supernatant as possible from the container containing the solid sample.
- 11.A.10 If a desorption experiment is not planned for a given sample, the concentration of the radionuclide in the solid fraction is obtained by taking an appropriate aliquot of the moist solid, weighing the aliquot, drying it at 105 degrees C, weighing the dried sample, and determining the amount of tracer in the solid using the appropriate analytical technique(s). Subtract the dry sample weight from the moist sample weight to obtain the water content of the sample.
- 11.A.11 If a desorption experiment is planned, follow procedure given in 11.A.10 but use an aliquot of 100-200 mg so that a sufficient amount of solid remains for the desorption experiment.
- 11.A.12 If further separation of solid from solution is to be accomplished by ultrafiltration go to step 11.A.16. If this separation is to be accomplished by centrifugation, follow steps 11.A.13 through 11.A.17.
- 11.A.13 centrifuge the aliquot taken in 11.A.8 at a minimum of 12,000 rpm for one hour using a Sorvall SS3 centrifuge or equivalent.
- 11.A.14 Take an appropriate aliquot of the supernate in item 11.A.13 and place in a clean container.
- 11.A.15 Continue the separation of the phases by centrifuging the aliquot taken in item 11.A.14 at a minimum of 12,000 rpm for two hours using the same centrifuge as used in 11.A.13.
- 11.A.16 Take an appropriate aliquot of the supernate from item 11.A.15 and place it in a clean container.

- 11.A.17 Continue the separation of the phases by centrifuging the aliquot taken in item 11.A.16 at a minimum of 25,000 rpm for at least 12 hours using a Sorvall OTD 65B Ultracentrifuge or equivalent and a Sorvall A-641 Rotor or equivalent. Go to step 11.A.19.
- 11.A.18 To complete the separation of the phases by ultrafiltration, take an appropriate aliquot of the liquid sample obtained in item 11.A.8 and separate the phases using an ultra-filter of appropriate pore size (e.g., Millipore CX-30; 100,000 MW). Follow manufacturers instructions on the use of the ultrafilter.
- 11.A.19 Take an appropriate aliquot of the liquid phases obtained in 11.A.17 or 11.A.18 and analyze it to determine the amount of tracer in this solution using the appropriate analytical technique.
- 11.A.20 Take the remaining aliquot of solution and determine its pH using procedure TWS-INC-DP-35. After completing the pH measurement have the solution analyzed for major and trace elements.

#### Notebook Entries

11.a. The following entries must be made in the laboratory notebook:

- 11.a.1 Identification number of balance used for weighing.
- 11.a.2 Volume or weight of the stock solution added to the pre-equilibrated crushed rock.
- 11.a.3 Julian date at the beginning of the experiment.
- 11.a.4 Weight of the container, dry solid sample, and stock solution added.
- 11.a.5 Amount (by weight or volume) of the aliquot of the initial stock solution analyzed and pH determined for this solution.
- 11.a.6 Length of equilibration time.
- 11.a.7 Weight of the container after equilibration.

11.a.8 If desorption is going to be effected, record weight of the container with the moist equilibrated solid sample. If the solid is to be analyzed for determination of the amount of tracer in the solid phase, record weight of the aliquot of the moist and dried solid.

11.a.9 Method used for separation of phases; if filtration is utilized record the pore size of the ultra-filter used. If centrifugation is used, record type of centrifuge and diameter of rotor. Also record the amount (by weight or volume) of the aliquot(s) of solutions analyzed in step 11.A.19.

11.a.10  $R_d$  value(s) calculated.

## 11.B. Desorption Procedure

11.B.1 Add a known amount of the water used in the sorption experiment to the sample prepared in 11.A.10 and record the Julian date. Weigh the container with the solid and the water.

11.B.2 Shake the container for three weeks or a more appropriate period depending on the specific experiment.

11.B.3 Follow steps 11.A.8 and 11.A.12 through 11.A.20 as appropriate.

## Notebook Entries

11.b. The following entries must be made in the laboratory notebook:

11.b.1 Identification number of balance used for weighing.

11.b.2 Volume or weight of the water added to the solid sample from the sorption experiment and Julian date at the beginning of the desorption experiment.

11.b.3 Weight of the container, equilibrated solid sample, and water added at the beginning of the desorption experiment.

11.b.4 Entries specified on items 11.A.5, 11.A.6, 11.A.7, 11.A.8, and 11.A.10.

## 12. POTENTIAL SOURCES OF UNCERTAINTY AND ERROR

Potential sources of error include the following:

- 12.1 Malfunctions in equipment (balances, counters, shakers, etc.)
- 12.2 Improper use of equipment.
- 12.3 Improper calibration or standardization of equipment.
- 12.4 Incomplete separation of solid and liquid samples.
- 12.5 Dissolution of solid sample during the experiment.
- 12.6 Leakage from the container during shaking or handling.
- 12.7 Misidentification or interferences in gamma-ray spectrum.
- 12.8 Improper recording or transfer of data.

### 13. METHOD OF DATA REDUCTION

Data reduction consists of simple addition and subtraction operations to obtain net weights and volumes and application of the equation in section 7. The concentration of the element(s) of interest in the solution phase are obtained directly from step 11.A.19. The mass or activity of the element(s) of interest in the solid are obtained by multiplying the volume of liquid (in ml) obtained in 11.A.10 or 11.A.11 times the concentration of the element(s) of interest (per ml) obtained in 11.A.19. This mass or activity is subtracted from the mass or activity of the element(s) of interest in the solid obtained in 11.A.10 or 11.A.11.

### 14. METHODS OF RECORDING AND STORING DATA AND RESULTS

Record the information required for preparatory verification (outlined in section 9) in the laboratory notebook. Record any special conditions used for sample preparation in the laboratory notebook (see section 10). Record the information specified in section 11 in the laboratory notebook.

### 15. SAMPLE/SITE TRACEABILITY

The traceability of the rock and mineral samples used in this procedure follows the procedure described in TWS-INC-DP-83. The crushed rock utilized will carry its unique identifier from TWS-INC-DP-63. The water utilized in the experiment will carry its unique identifier from TWS-INC-DP-62.

## QUALITY ASSURANCE REQUIREMENTS

### 16. ACCEPTANCE/REJECTION CRITERIA FOR DETERMINING THAT ACTIVITIES HAVE BEEN SATISFACTORILY ACCOMPLISHED

All batch sorption experiments will be done in duplicate. If sorption ratios obtained in duplicate experiments vary by more than a factor of 2, the experiments must be repeated.

Verify that all necessary information for the sorption and desorption experiments specified in section 11 is recorded in the laboratory notebook.

### 17. HANDLING, SHIPPING, AND STORAGE REQUIREMENT

No special requirements are necessary for samples used in this procedure.

### 18. IDENTIFICATION OF QA RECORDS TO BE GENERATED AND THEIR CONTROL

The records produced by this procedure will be recorded in the investigator's laboratory notebook. The data obtained will be published in accordance with LANL Policy and TWS-QAS-QP-03.2.

### 19. TRAINING REQUIREMENTS AND METHODS

Staff members and technicians assigned to this work will be qualified by formal on-the-job training under the supervision of qualified personnel according to TWS-QAS-QP-2.7.

### 20. CALIBRATED INSTRUMENTATION INFORMATION

The balance(s) used must be calibrated according to TWS-QAS-QP-12.1. The tolerance on the speed of the centrifuges is sufficiently large so they do not need calibration.

## 21. PROVISION FOR DOCUMENTATION, REPORTING, AND EVALUATION OF PROCEDURAL DEVIATION

Unplanned deviations from this procedure will be documented in the notebook. The responsible PI or his designee will make a determination as to whether to use the data affected by the deviation. If a decision to use the data is made, the justification for this decision must be entered in the investigator's laboratory notebook.

## 22. SUBJECTS REQUIRING VERIFICATION

The recording of the information specified in section 9 needs to be verified before initiating the experiment.

## 23. APPENDIX AND/OR ATTACHMENTS

None

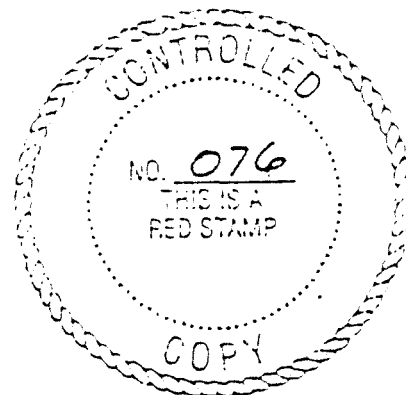
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# SORPTION AND DESORPTION DETERMINATIONS BY A BATCH SAMPLE TECHNIQUE FOR THE DYNAMIC TRANSPORT TASK



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Los Alamos

Yucca Mountain Site

Characterization Project

Los Alamos  
Yucca Mountain Site  
Characterization Project



# SORPTION AND DESORPTION DETERMINATIONS BY A BATCH SAMPLE TECHNIQUE FOR THE DYNAMIC TRANSPORT TASK

## 1.0 PURPOSE

The purpose of this procedure is to delineate a method for determining sorption and desorption coefficients for the distribution of various species between geologic materials and natural and synthetic waters. The Dynamic Transport Task uses mostly columns of different configurations to determine the characteristics of the geologic media.

## 2.0 SCOPE

This procedure can define guidelines to be used for sorption and desorption studies in the tasks of the LANL YMP.

## 3.0 REFERENCES

- 3.1 TWS-QAS-QP-03.5 "Procedure for Documenting Scientific Investigations"
- 3.2 LANL-YMP-QP-06.3 "Preparation, Review, and Approval of Detailed Technical Procedures"
- 3.3 TWS-QAS-QP-12.1 "Procedure for Control of Measuring and Test Equipment"
- 3.4 TWS-INC-DP-35 "pH Measurements"
- 3.5 TWS-INC-DP-62 "Bulk NTS Well Water Samples"
- 3.6 TWS-INC-DP-63 "Preparation of NTS Core Samples for Crushed Rock Experiments"
- 3.7 TWS-INC-DP-83 "Storage and Handling of Solid Samples"

## 4.0 DEFINITIONS

The measured sorption or desorption ratio,  $R_d$ , is defined as

$$R_d = \frac{\text{amount of the sorbing or desorbing species per g of solid}}{\text{amount of the sorbing or desorbing species per ml of solution}}$$

Tracer solution = solution containing element(s) whose sorption behavior is to be studied.

Ultra speed centrifuge = centrifuge capable of achieving a maximum speed of at least 65,000 rpm.

Super speed centrifuge = centrifuge capable of achieving a maximum speed of at least 20,000 rpm.

## 5.0 RESPONSIBILITIES

The PI has the responsibility for all operations. He/she may assign appropriate tasks to personnel trained to this DP. It is the responsibility of the users of this DP to adhere to the procedure. Investigators may direct deviations from the procedure upon approval of the responsible PI. It is the responsibility of the user to document such deviations in accordance to TWS-QAS-QP-03.5. It is the responsibility of the users of this DP to report unplanned deviations from this procedure to the responsible PI.

## 6.0 PROCEDURE

The trained user of this DP will follow the steps listed in sections 6.3, 6.4, and 6.5 to conduct a batch sample experiment. All data recorded at each step is to be recorded in a laboratory notebook pursuant to TWS-QAS-QP-03.5.

### 6.1 Principle

This procedure can be used to study sorption or desorption in the Dynamic Transport Task of the LANL YMP. This procedure can be utilized to measure a sorption ratio. If sorption equilibrium is attained during the experiment, the measured ratio is the distribution coefficient.

### 6.2 Equipment and Hardware/Software

Containers with a leak-proof cap must be used for sample containment. A shaker is used to equilibrate the samples. Ultra- and super-speed centrifuges and/or membrane-type filters are utilized to separate the solid from the liquid phases after equilibration. Centrifuge rotors must be capable of withstanding the velocities used for centrifugation. Calibrated balances must be used for determining weights in this detailed procedure. Analytical pipets must be used to measure volume quantities in this procedure.

6.2.1 If a malfunction of equipment occurs during this procedure the experiment is terminated.

6.2.2 The samples generated by this procedure can be radioactive; therefore, they should be handled in accordance with any applicable LANL safety procedure. The centrifuges must be operated in accordance with the manufacturer's instructions.

### 6.3 Preparatory Verification

#### 6.3.1 Hold Points

There are no hold points for this procedure.

#### 6.3.2 Calibration

Balances used for weighing are required to be calibrated pursuant to TWS-QAS-QP-12.1. When data are collected from a balance, the unique identifier number of that balance is recorded in the user's laboratory notebook along with the data collected. No other equipment requiring calibration is used in this procedure.

### 6.3.3 Environmental Conditions

No special environmental conditions are required for this DP. If any special conditions are utilized, they will be recorded in accordance with section 6.7 of this DP.

## 6.4 Control of Samples

All samples will be controlled using the following procedures:

- TWS-INC-DP-62 "Bulk NTS Well Water Samples"
- TWS-INC-DP-63 "Preparation of NTS Core Samples for Crushed Rock Experiments"
- TWS-INC-DP-83 "Storage and Handling of Solid Samples"

## 6.5 Implementing Procedure

### Experimental Steps for Data Acquisition

- 6.5.1 Clean the containers to be used for the experiment. The containers are usually cleaned by rinsing with deionized water three times and drying without permitting contamination. Deviation from this cleaning routine will be documented in section 6.7 of this procedure.
- 6.5.2 Weigh an amount of the material to be used into a cleaned container. Determine the weight of the container with the material to be used.
- 6.5.3 Add a known volume of the water to be used in the experiment to the container from item 6.5.2. Determine the weight of the container after addition of the water.
- 6.5.4 Shake the mixed phases. Normally the pre-equilibration step is performed for a period from 2-14 days.
- 6.5.5 Centrifuge the mixture for at least 2 hours at a minimum speed of 5,000 rpm.
- 6.5.6 Separate the phases (by decanting or pipetting the solution).
- 6.5.7 Determine the weight of the container from item 6.5.6.
- 6.5.8 Prepare the tracer solution to be used for this experiment and document the method used in the notebook.
- 6.5.9 Add a known volume or weight of the tracer to the pre-equilibrated material, record the julian date. Determine the weight of the container, moist material and tracer solution added.

- 6.5.10 Take an aliquot of the tracer solution and analyze it using the appropriate analytical technique, to determine the initial concentration of the tracer in the solution used. Take a second aliquot to determine the pH of the tracer solution following TWS-INC-DP-35.
- 6.5.11 Shake the container in item 6.5.9. Usually the container(s) is shaken for three weeks. If a different length of time is utilized, the deviation will follow section 6.7 of this DP.
- 6.5.12 After equilibration, weigh the container.
- 6.5.13 Separate the phases by filtration using a membrane-type filter of appropriate size or by centrifuging the sample(s) for one hour at a minimum of 5,000 rpm. After separation, take an aliquot of the filtrate (if filtration is used) or the supernatant (if centrifugation is used) and transfer to a clean container.
- 6.5.14 If desorption is going to be performed, remove the remaining supernatant, weigh the container with the moist material, and follow the desorption procedure. If the solid is going to be analyzed for determination of the amount of tracer in the solid phase, remove the remaining supernatant, take an aliquot of the moist material, weigh the aliquot, let dry, weigh the dried sample, and determine the amount of tracer in the solid using the appropriate analytical technique.
- 6.5.15 If separation is performed by filtration in step 6.5.13, use a portion of the filtrate for pH determination following TWS-INC-DP-35 and proceed to step 6.5.16. If separation is performed by centrifugation, proceed as in steps 6.5.13 through 6.5.18.
- 6.5.16 Continue the separation of the phases by centrifuging the aliquot taken in step 6.5.13 at a minimum of 12,000 rpm for one hour.
- 6.5.17 Take an aliquot of the centrifuged sample in step 6.5.16 and place in a clean container.
- 6.5.18 Continue the separation of the phases by centrifuging the aliquot taken in step 6.5.17 at a minimum of 12,000 rpm for two hours.
- 6.5.19 Take an aliquot of the centrifuged sample in step 6.5.18, place it in a clean container, and analyze it to determine the amount of tracer in the solution using the appropriate analytical technique. The remaining solution is used for pH determination following TWS-INC-DP-35.

## 6.6 Data Acquisition and Reduction

Calculate the  $R_d$  according to the definition given in section 4.0. This calculation can be performed directly if the amount of tracer in the solid phase has been measured. The calculation can also be performed by difference using the tracer concentrations in the initial and tracer-contacted solutions in order to determine the amount of the tracer that abandoned the solution and is present in the solid phase.

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#### 6.7 Deviations From the DP and Potential Sources of Error and Uncertainty

Any deviations from this procedure will be documented in the user's laboratory notebook. If the deviation is deemed critical by the PI, then a written statement will be put into the user's laboratory notebook evaluating the potential source of error and uncertainty.

#### 7.0 RECORDS

Records resulting from the proper execution of this DP are entries in the laboratory notebooks.

#### 8.0 ACCEPTANCE CRITERIA

As long as this DP is followed and no critical deviation (see section 6.7) is made, this data will be accepted as qualified data for the YMP.

#### 9.0 TRAINING

Staff members and technicians assigned to this work will be qualified by formal "hands on" training under the supervision of qualified personnel.

#### 10.0 ATTACHMENTS

None.

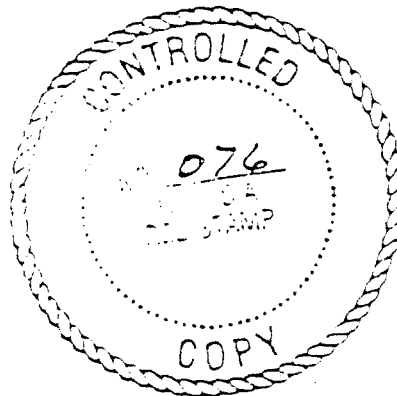
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## CRUSHED ROCK COLUMN STUDIES



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Los Alamos

Yucca Mountain Site  
Characterization Project

## HISTORY OF REVISIONS

[illegible]

# Los Alamos

## Yucca Mountain Site

## Characterization Project

## Crushed Rock Column Studies

### 1.0 PURPOSE

This detailed technical procedure (DP) describes dynamic transport tests on crushed rock columns by studying the flow of a known tracer with a known flow rate through a column of crushed rock for the Yucca Mountain Site Characterization Project (YMP).

### 2.0 SCOPE

This DP applies to all YMP personnel who assemble, prepare, and sample crushed rock columns within the Dynamic Transport Task of the Los Alamos National Laboratory (Los Alamos) YMP.

### 3.0 REFERENCES

TWS-QAS-QP-03.5, Procedure for Documenting Scientific Investigations  
LANL-YMP-QP-12.1, Procedure for Control of Measuring and Test Equipment  
LANL-INC-DP-35, pH Measurements  
TWS-INC-DP-62, Bulk NTS Well Water Samples  
TWS-INC-DP-63, Preparation of NTS Core Samples for Crushed Rock Experiments  
TWS-INC-DP-83, Storage and Handling of Solid Samples

### 4.0 DEFINITIONS

#### 4.1 Tracer solution

The tracer solution is the solution containing the substance(s) whose diffusion behavior is to be studied.

#### 4.2 Eluate

The eluate is the solution resulting from an elution process.

#### 4.3 Collection time

The collection time is the time interval between collection of eluate samples.

#### 4.4 Flow rate

The flow rate is the amount of liquid eluted through the column per unit of time.



#### 4.5 $c_0(t)$

The tracer concentration in initial tracer solution in time (i.e., the aliquot of the initial tracer solution taken at the beginning of the experiment) corresponds to  $C_0(t=0)$ .

#### 4.6 $c_i(t)$

The tracer concentration in solution i at time t (solution i represents the eluate collected during time t).

### 5.0 RESPONSIBILITIES

#### 5.1 Principal Investigator (PI)

The PI has overall responsibility for work performed under this DP, ensures that each user is trained, recommends and directs variations when appropriate, and determines the acceptability of data. The PI may assign portions of these tasks to appropriate personnel trained to the DP.

#### 5.2 Users

YMP personnel who use this DP are responsible for adhering to the procedures described in it and for documenting deviations from this procedure in accordance with QP-03.5.

### 6.0 PROCEDURE

#### 6.1 PRINCIPLE

This procedure describes the set up and proper conduct of crushed rock column experiments. Results are used to evaluate batch sorption measurements under flowing conditions. By comparing differences between batch measurements and crushed rock column measurements, one will be able to study multiple species formation, colloid formation, and other geochemical reactions.

#### 6.2 EQUIPMENT AND HARDWARE/SOFTWARE

Equipment needed is listed below. Items equivalent to those listed below may be used provided they perform the same function with an acceptable level of performance as judged by the user or the PI.

- 260 ML Isco syringe pump or 60 ML syringe pump
- calibrated balance
- commercially available measuring tools (i.e., tape measure, ruler, micrometer, or caliper)
- Luer fittings w/frits, tubing
- Rheodyne injection valve

- Polyether Etherketone (PEEK) or teflon tubing
- Polyethylene frits and Luer fittings
- fraction collector vials
- test tubes

#### 6.2.1 Equipment Malfunctions

The equipment used to implement this procedure shall be in good repair before the experiment is started.

#### 6.2.2 Safety Considerations

The equipment required to carry out this procedure shall be used in accordance with any applicable Los Alamos safety procedure.

### 6.3 PREPARATORY VERIFICATION

There are no critical setup parameters, prerequisites, or mandatory verification points.

#### 6.3.1 Hold Points

There are no hold points for this procedure.

#### 6.3.2 Calibration

6.3.2.1 Balances used for weighing are required to be calibrated pursuant to QP-12.1. When data are collected from a balance, the unique identifier number of that balance is recorded in the user's laboratory notebook along with the data collected.

6.3.2.2 All pH determinations shall be conducted in accordance with DP-35. The unique identifier of the pH meter shall be recorded in the user's laboratory notebook.

6.3.2.3 The measuring instruments used (i.e., tape measure, ruler, caliper, or micrometer) are commercial-grade and do not require calibration pursuant to QP-12.1.

#### 6.3.3 Environmental Conditions

No special environmental conditions are required for this DP. If any special conditions are used, they will be recorded according to Section 6.7 of this DP.

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#### 6.4 CONTROL OF SAMPLES

All samples will be controlled according to DP-83, Storage and Handling of Solid Samples.

#### 6.5 IMPLEMENTING PROCEDURE

6.5.1 Prepare the crushed rock according to directions in DP-63.

6.5.2 Prepare the column.

6.5.2.1 Make the column from acrylic or teflon tubing with end caps machined from polyether Etherketone (PEEK) material. Polyethylene frits are utilized in the end caps to hold in the material.

6.5.2.2 Measure the length of the column to within 0.25 in., using a tape measure or ruler. Record value in notebook.

6.5.2.3 Weigh the empty column. Record value in notebook.

6.5.3 Prepare the tracer solution

6.5.3.1 Prepare a solution of the appropriate ground water containing the tracer(s) to be used. The source of the ground water and tracer(s) are specified by the PI. Record the type of tracer and the method of preparation in the notebook.

6.5.3.2 Measure the pH of the solution according to DP-35 and record in the notebook.

6.5.3.3 Place an aliquot of the tracer solution in a capped container (the tracer concentration of this aliquot will be used to determine the initial concentration of the tracer).

6.5.4 Pack the column with either dry or wet crushed rock.

6.5.4.1 For a dry packed column, pour the rock into the column through the funnel. If necessary, tap or vibrate column to make the rock reach the bottom of the column. Some banding may appear as a result of differences in particle densities; small, numerous bands are desirable. If the banding is too wide, remove the rock from the column and then pack again. Remove the funnel and replace it with an end cap and frit. If settling occurs when water is pumped through the column, remove the top Luer fitting and frit, replace the funnel, and add more crushed rock. Weigh the packed column and record weight in the notebook.

- 6.5.4.2 For a wet packed column, pour a slurry of crushed rock and water into the funnel. When the column is full, remove the funnel and attach an end cap and frit. If settling occurs, remove the top end cap and frit, replace the funnel, and add more crushed rock. Weigh the packed column and record value in the notebook.
- 6.5.5 Prepare the pump by filling it with the appropriate ground water, as specified by the PI. Check all the connections from the pump to the injection valve (i.e., the injection valve loop, from the injection valve to the column, and from the column to the collection vessel).
- 6.5.6 Place the pre-weighed vials to be used for eluate collection in the fraction collector. Check injection vessel or collection vials for correct loading in the fraction collector. Record weights and vials in sequence.
- 6.5.7 Determine the flow rate through the column. Weigh ten or fifteen test tubes and record the weights. Pump a definite volume of water through the column for a fixed period of time and collect in each of the tubes. Weigh the tubes again and record the weight of each tube. The flow rate is determined from the weight of the water in each tube and the time of collection.
- 6.5.8 Ensure that the following data are recorded in a notebook:
- Unique identifier of the sample used to prepare the column (carried from the procedure DP-63). If more than one column has been prepared from the same NTS sample, an additional alphanumeric character will be added to the identifier in order to maintain uniqueness.
  - The length and diameter of the crushed rock column.
  - The weight of empty column.
  - The weight of packed column, dry packed or wet packed.
  - The unique identifier of the water used (carried from DP-62).
  - The tracer solution to be used and analytical method of preparation (e.g., the experimental steps used for preparation, notebook TWS number and pages used specifying these steps, or a detailed procedure).
  - The unique identifier of analytical balance used.
  - The flow rate through the crushed rock column.

- The volume of tubing from syringe or valve to column.
- The volume of tubing from column to collection vessel.

6.5.10 Conduct the experiment

- 6.5.10.1 Load the traced solution in the injection valve loop.
- 6.5.10.2 Turn the injection valve to *inject* and turn on the fraction collector for vial collection or insert the tube into the collection vessel.
- 6.5.10.3 Record the date and time.
- 6.5.10.4 Place an aliquot of the tracer solution in a container (the tracer concentration of this aliquot will be used to determine  $C_0$  at an arbitrary time  $t$ ).
- 6.5.10.5 Ensure that the following entries are recorded in a laboratory notebook:
- The volume of the injection loop.
  - The start time of eluate collection and amount of initial tracer solution to be analyzed, specifying the units of volume or weight used for measuring amount.
  - The start time of the injection.
  - The tare weight and total weight of each vial.
  - The ID# of analytical balance used.
  - The analytical technique used and a reference to the detailed procedure used for this technique.
  - The collection time to be used on fraction collector.
- 6.5.10.6 At the conclusion of the experiment (determined by the PI based on the analytical results of the periodic samples), determine the pH (according to DP-35) of the solution in the non-tracer reservoir and record the data in the notebook.

## 6.6 DATA ACQUISITION AND REDUCTION

The tare and the final weight of eluate vials are later reduced by subtracting the tare weights from final weights of the collection vials and dividing by the elapsed time in order to obtain the flow rate of the column. The relative concentration of the tracer,  $C_i(t)/C_o(t)$ , will be calculated for each eluate collected.

## 6.7 DEVIATIONS FROM THE DP AND POTENTIAL SOURCES OF ERROR AND UNCERTAINTY

Any deviations from this procedure will be documented in the user's notebook. If the deviations are deemed critical by the PI, a written statement will be put into the user's laboratory notebook evaluating the potential source of error and uncertainty.

The most common source of error that results in data rejection is leakage of the column. Leakage can be caused by loose Luer connectors. Leakage is detected by periodic visual inspection. If leakage is detected, record this problem in the laboratory notebook and reject the data.

Evaporation of the tracer in the collection vials can cause errors in the results. Consequently, keep the collection vials capped after eluate collection.

## 7.0 RECORDS

Records resulting from the proper execution of this DP are entries in the laboratory notebooks and QA approved software. Electronic data shall be documented according to QP-03.5.

## 8.0 ACCEPTANCE CRITERIA

Proper recording of the data specified in Sections 6.5.8 and 6.5.10.6 constitute the acceptance criteria for this DP. If no critical deviations (see Section 6.7) were made, these data will be accepted as qualified data for YMP.

## 9.0 TRAINING

The PI or his designee will formally train the users assigned to implement this DP. The training will require observation and evaluation of the performance of the trainee as he follows this DP.

## 10.0 ATTACHMENTS

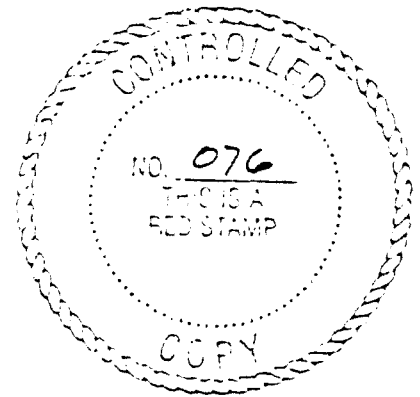
None.

UNCONTROLLED

TWS-ENC-DP-88, R1

STORAGE AND HANDLING OF SOLID SAMPLES

Effective Date: 10/10/90



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## 6.0 PROCEDURE

### 6.1 Sample Inventory Logbook

The Sample Inventory Logbook is a notebook and any associated binders that is dedicated to recording or logging the receipt, origin, location, analytical results (if appropriate), and current custodian (if the samples are not in the storage area) of solid samples used in the YMP at TA-48.

#### 6.1.1 Logbook entries

Entries in the logbook must conform with the requirements of the procedure for scientific investigations (TWS-QAS-QP-03.5, which requires all entries to be initialed and dated) and should follow a consistent format. One page of the book should be devoted to each sample; the first several pages of the logbook should be a table of contents that indicates the page number(s) that is (are) dedicated to an individual sample. On the sample page, the initial entry should indicate the origin of the sample; for procured materials, this would be a simple reference to the purchase request number. For synthesized materials, the origin entry should reference the notebook number and page that describes the procedure that was used to create the material. Subsequent entries should represent a chronology of the history of the material, including who took custody of the material, when it was moved to another location, when it was depleted in experiments, and references to the binder that contains copies of any analytical results or other pertinent records.

#### 6.1.2 Logbook binder

Separate loose-leaf binder(s) are considered part of the Sample Inventory Logbook and are used to contain separate copies of analytical results and/or other tests performed on solid materials. Each page added to the binder(s) must be clearly numbered in the upper corner and listed on the table of contents pages in the front of the binder.

### 6.2 Receipt of solid samples

When solid material is received (from a supplier, from the YMP Sample Management Facility, from another investigator, or from an investigator who synthesized it), it will either be transferred directly to the appropriate laboratory for use or it will be stored in the sample storage area.

All samples or specimens received at TA-48 from the Yucca Mountain Project Sample Management Facility (see Yucca Mountain Project Office procedures AP-6.3 and AP-6.4) must have the required bar code or other labels attached (either to the sample or container) and must be logged into the Sample Inventory Logbook. Solid materials purchased for YMP or synthesized in a laboratory should be logged into the logbook, but are not required to be logged in if the material is intended only for a specific task or use in a single laboratory. In such cases, the records of origin and chain-of-custody documentation must be kept by the responsible PI.

### 6.3 Sample Storage area

A suitable area in the laboratory will be assigned to the project for sample storage. The storage cabinets in this area will be kept locked; the individuals (at least two) who have keys to the cabinets will be listed on the cabinets. The storage area will not be used to store materials that are not logged into the Sample Inventory Logbook.



## STORAGE AND HANDLING OF SOLID SAMPLES

## 1.0 PURPOSE

The purpose of this detailed technical procedure (DP) is to describe the storage and handling of solid (eg., rock and mineral) samples at TA-48 for the Yucca Mountain Project (YMP). The samples used in YMP experiments need chain-of-custody documentation and appropriate storage facilities to ensure their integrity and traceability.

## 2.0 SCOPE

This procedure applies to all Los Alamos National Laboratory (LANL) personnel who work at TA-48 and who use solid samples in YMP activities.

## 3.0 APPLICABLE DOCUMENTS

LANL-YMP-Quality Assurance Program Plan (QAPP)

TWS-QAS-QP-02.7, Personnel Training

TWS-QAS-QP-03.5, Procedure for Documenting Scientific Investigations

TWS-QAS-QP-08.1, Procedure for Identification and Control of Samples

TWS-QAS-QP-13.1, Procedure for Handling, Shipping, and Storage

TWS-QAS-QP-17.3, Procedure for LANL YMP Records Management

YMP-AP-06.3Q, Interaction of Participants and Outside Interests with YMP Sample Management

YMP-AP-06.4Q, Procedure for the Submittal, Review and Approval of Requests for YMP Geologic Specimens

## 4.0 DEFINITIONS

- 4.1 solid samples: solid materials intended for laboratory studies that were obtained directly from the Yucca Mountain area, obtained from special sources (eg., mineral localities or chemical suppliers), or were synthesized in the laboratory. Such solid samples represent minerals or other solids associated with Yucca Mountain (see TWS-QAS-QP-08.1 for further discussion).
- 4.2 chain-of-custody documentation: written documentation showing the transfer of samples from their point of origin to their usage in a given experiment and, if appropriate, their return to storage or to other personnel.

## 5.0 RESPONSIBILITIES

## 5.1 Principal Investigator

The PI has the responsibility for the proper storage and handling of solid samples. He may assign this task to appropriate personnel trained to this DP.

## 5.2 Users and handlers of solid materials at TA-48

It is the responsibility of the users of this DP to adhere to the procedure. Any deviations from this procedure require approval from the responsible PI. It is the responsibility of the user to document such deviations in accordance with TWS-QAS-QP-03.5. It is the responsibility of the users of this DP to report unplanned deviations from this procedure to the responsible PI.

Any special environmental conditions required for sample storage must be provided by the responsible PI. The location where such special samples are kept must be recorded in the logbook.

#### 6.4 Unused material

Unused sample material remaining after the completion of an experiment or set of experiments should be returned to the storage area, but the prior handling and contact must be identified in the logbook.

### 7.0 QUALITY ASSURANCE DOCUMENTATION

#### 7.1 Records

Records to be generated as a result of the proper execution of this DP are entries in the Sample Inventory Logbook.

### 8.0 ACCEPTANCE CRITERIA

The criteria that show this procedure has been correctly implemented are the records identified in Section 7.1.

### 9.0 ATTACHMENTS

None.

### 10.0 TRAINING REQUIREMENTS AND METHODS

Acceptable training methods for this procedure include reading the procedure or on-the-job training. In accordance with the training procedure (TWS-QAS-QP-02.7), the author, PI, and reviewer are considered trained to this DP. YMP personnel who receive, store, handle, and transfer samples covered under the scope of this DP must be trained to it. Training of personnel to this DP is documented in accordance with the training procedure.

### 11.0 SUBJECTS REQUIRING VERIFICATION

The identifier numbers or letters found on the samples upon receipt must be verified with the enclosed documents or with the previously received documentation. These numbers must be recorded in the Sample Inventory Logbook.

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## APPENDIX D

# COLLECTED RADIOCHEMICAL AND GEOCHEMICAL PROCEDURES

UNCONTROLLED

LA-1721, 5th Ed.

UC-701 and UC-703  
Issued: May 1990

*Collected Radiochemical and  
Geochemical Procedures*

*Fifth Edition*

*Compiled and Edited by  
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*Individuals responsible for developing procedures are named at the  
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# SEPARATION OF URANIUM AND PLUTONIUM FROM LARGE SAMPLES OF UNDERGROUND DEBRIS

H. L. Smith and G. W. Knobeloch

## 1. Introduction

This procedure was devised for the separation of uranium and plutonium from solutions of high ionic strength, which were obtained by dissolving underground nuclear debris. In the separation, these elements are oxidized to the +6 state and extracted into diethyl ether from a solution saturated with  $\text{NH}_4\text{NO}_3$  and  $\sim 2M$  in  $\text{HNO}_3$ . The extraction is an excellent decontamination step because very little else is taken into the ether. The uranium and plutonium are back-extracted into water and the aqueous solution is evaporated to dryness. Then the procedure for the SEPARATION OF URANIUM AND PLUTONIUM FROM UNDERGROUND NUCLEAR DEBRIS FOR MASS SPECTROMETRIC ANALYSIS is performed.

## 2. Reagents

$\text{HNO}_3$ : fuming  
 $\text{HClO}_4$ : conc  
 $\text{NH}_4\text{NO}_3$ : solid  
Diethyl ether

## 3. Procedure

*Step 1.* Transfer the sample in  $\text{HCl}$  and  $\text{HClO}_4$  to an erlenmeyer flask of suitable size. Add a volume of fuming  $\text{HNO}_3$  that is equivalent to  $\sim 10\%$  of the sample volume; heat carefully on a hot plate for several hours, and boil to dryness to drive off all the  $\text{HClO}_4$ .

*Step 2.* Add  $\sim 50$  ml of fuming  $\text{HNO}_3$  and evaporate to dryness again. Heat the sides of the flask to expel any residual  $\text{HClO}_4$ .

*Step 3.* Dissolve the residue in  $\sim 40$  ml of fuming  $\text{HNO}_3$ ; warm if necessary. Transfer the solution to 40-ml glass centrifuge tubes and centrifuge out any insoluble residue (Note 1).

*Step 4.* Transfer the supernate to a 1-l beaker, dilute with  $\text{H}_2\text{O}$  to make the solution  $\sim 2M$  in  $\text{HNO}_3$ , and add solid  $\text{NH}_4\text{NO}_3$  until the solution is saturated with that reagent. Transfer to a separatory funnel and extract twice with equal volume portions of diethyl ether (Note 2). Combine the ether phases in a clean separatory funnel.

*Step 5.* Back-extract with three portions of  $\text{H}_2\text{O}$ , each equivalent in volume to  $\sim 10\%$  of the combined ether phases. Combine the aqueous extracts and begin with Step 1 of the procedure for the SEPARATION OF URANIUM AND PLUTONIUM FROM UNDERGROUND NUCLEAR DEBRIS FOR MASS SPECTROMETRIC ANALYSIS.

## Notes

1. If the residue shows no activity, it may be discarded. If, however, it contains a substantial fraction of the total activity in the sample, an attempt should be made to bring the active substances into solution. Heating with  $6M$   $\text{NaOH}$ , followed by acidification with  $\text{HNO}_3$ , will usually remove most of the activity from the precipitate.

2. Isopropyl ether is not satisfactory as an extractant.

(October 1989)

# PLUTONIUM

D. C. Hoffman

## 1. Introduction

This procedure for plutonium depends upon the almost-quantitative carrying of plutonium(IV) on  $\text{LaF}_3$  and the great difference between adsorption of plutonium(III) and that of plutonium(IV) in 12M HCl medium on a Dowex A-1 anion-exchange resin. One cycle of the procedure serves to separate plutonium from other alpha-emitters; two cycles usually give complete decontamination from beta-emitting fission products.

The initial  $\text{LaF}_3$  precipitation, carried out in the presence of  $\text{NH}_2\text{OH}$ , is an excellent volume-reducing step and also eliminates many elements (notably iron) that may interfere in the subsequent adsorption of plutonium on the resin column. After dissolution of the  $\text{LaF}_3$  precipitate in 12M HCl, neptunium, plutonium, and any traces of iron and uranium are adsorbed on the anion resin column, whereas the lanthanides, americium, and curium pass through the column. Plutonium is eluted from the column after reduction to plutonium(III) with HI; neptunium is not reduced to the +3 state and remains behind. (A solution that contained 15  $\mu\text{g}$  of  $^{235}\text{U}$  was run through the procedure, and no fission counts above the usual background of 0.1 to 0.2 ng could be detected.)

The plutonium is collected directly from the resin column on 1  $\frac{7}{8}$ -in. platinum disks that are flamed, alpha-counted, and, if necessary, pulse-analyzed. The plates are usually very clean and may be alpha-pulse-analyzed with a resolution of 1 to 1.5%.

Samples may be run in quadruplicate and yields are usually determined in one of two ways. Enough  $^{236}\text{Pu}$  tracer to equal 25 to 50% of the total plutonium alpha-activity expected may be added to one or two of the original aliquots. On completion of the analysis, the fraction of  $^{236}\text{Pu}$  in the sample is determined by pulse analysis, and the yield is

calculated. Yields may also be determined by spiking two of the four samples with a standardized solution of plutonium activity that is at least five times as active as the aliquot to be analyzed. The average number of counts per minute in the two unspiked samples is subtracted from the average in the two spiked samples. The resulting value, divided by the number of counts per minute in the spike, gives the yield. The chemical yield is usually ~97%; for a set of four aliquots analyzed simultaneously, this value is constant to within  $\pm 1\%$ . In analysis of solutions of very high ionic strength, the yields are somewhat lower (90 to 97%), probably because under these conditions the  $\text{LaF}_3$ -carrying step is less efficient.

## 2. Reagents

Lanthanum carrier: 5 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

$^{236}\text{Pu}$ : standardized solution in 3M HCl; or standardized spike solution (any mixture of plutonium isotopes in 3M HCl)

HCl: conc; 3M

HF: conc

HF- $\text{HNO}_3$ : equal volumes of 2M solutions

$\text{HNO}_3$ : conc

$\text{H}_3\text{BO}_3$ : saturated aqueous solution

$\text{NH}_2\text{OH} \cdot \text{HCl}$ : 35% by weight in  $\text{H}_2\text{O}$ ; solid

Solution I: 0.1 ml conc  $\text{HNO}_3$ /15 ml conc HCl

Anion-exchange resin: AG 1-X10, 200 to 400 mesh; slurry in  $\text{H}_2\text{O}$

HI stock solution: Distill HI (Mallinckrodt analytical reagent-grade, 5.5M in HI, 1.5%  $\text{H}_3\text{PO}_2$  preservative) under nitrogen. The HI cannot be used without distillation because  $\text{H}_3\text{PO}_2$  preservation apparently causes the eluted drops to attack the platinum collection disks and make the samples unsuitable for pulse analysis. Commercial preparations of HI without preservative usually contain so much free iodine that they are unsuitable. Even after being stored under nitrogen, distilled HI is slowly oxidized. Oxidation is inhibited by the addition of sufficient hydrazine (up to 20% by volume of 64 to 84%  $\text{N}_2\text{H}_4$  in  $\text{H}_2\text{O}$ ) to

decolorize the HI solution. The final solution is  $\sim 4.4M$  in HI.

HI-HCl eluant: 1 ml of HI stock solution is added to 7 ml of conc HCl to give a solution  $\sim 0.44M$  in HI. The precipitate that results from the hydrazine present is removed by centrifugation; the supernate is saturated with gaseous HCl. The solution is permitted to come to equilibrium at room temperature before use; because the solution is readily oxidized, fresh reagent is required every few days.

### 3. Procedure

*Step 1.* Pipette 1 ml of tracer or spike solution into 40-ml long-taper, glass centrifuge tubes that will hold samples on which yield is determined. Pipette sample ( $3M$  in HCl) into each centrifuge tube; use 1-ml aliquots if possible, although aliquots as large as 25 ml can be used if necessary. Bring all solutions to the same volume by adding to those that do not contain tracer (or spike) acid of the same concentration as that in the tracer (or spike).

*Step 2.* To each tube add 1 to 2 drops of lanthanum carrier/ml of solution and then stir. Add 4 to 5 drops of  $N_2HOH \cdot HCl$ /ml of solution and stir. Add 3 drops of conc HF/ml of solution (Note 1), stir, and let stand for 5 min (Note 2).

*Step 3.* Centrifuge and discard the supernate.

*Step 4.* Wash the precipitate with 10 drops of  $2M HF$ - $2M HNO_3$ . Stir, centrifuge, and discard the supernate.

*Step 5.* Dissolve the  $LaF_3$  precipitate by adding 2 to 3 drops of saturated  $H_3BO_3$  solution, stirring, and then adding 0.5 ml of conc HCl while stirring. If the solution is clear and colorless, continue adding conc HCl until the volume of solution is 2 ml. Add 1 drop of conc  $HNO_3$  and heat gently. The solution is now ready for Step 6. If, after treatment with

conc HCl, the solution is yellow—even faintly so—dilute to 2 ml with  $H_2O$ ; omitting the addition of lanthanum carrier, repeat Steps 2 through 5.

*Step 6.* Transfer the solution to a 3- to 5-cm by 4-mm Dowex AG-1 resin column that has been washed with  $\sim 1$  ml of Solution I (Note 3). (This wash may be driven through the column with air pressure.) By means of air pressure, push the solution that contains the sample through the column. Wash the centrifuge tube with two 1-ml portions of Solution I and discard the washes.

*Step 7.* Wash the sides of the centrifuge tube with 1.5 ml of conc HCl, stir with a stirring rod, and remove the rod. Centrifuge the HCl wash and pass the solution through the resin column under pressure.

*Step 8.* Add a few crystals of  $N_2HOH \cdot HCl$  directly to the top of the resin column. Wash the centrifuge tube with 1 ml of conc HCl, transfer the wash to the top of the column and push it through with pressure. Do not let the column run dry under pressure because air bubbles will be forced into the column and will cause channeling and erratic elution of activity.

*Step 9.* Transfer  $\sim 1$  ml of HI-HCl eluant to the top of the column, but apply no pressure during elution. The dark band of the eluant may be seen migrating down the column. Start collecting the drops around the edge of 1  $\frac{7}{8}$ -in. platinum disk when the band is halfway down the column. After the band reaches the bottom of the column, collect 15 drops of eluant, and place as many of them as possible in the center of the disk. If necessary, collect the rest on top of the drops already around the edge of the disk.

*Step 10.* Place the disk on a hot plate (setting  $\sim 400$ ) under a heat lamp and allow the drops to evaporate. Heat the disk to red heat in an open flame and then cool. Alpha-count if the original aliquot was spiked; pulse-analyze and alpha-count if  $^{236}Pu$  tracer was used. (Notes 4 and 5).

## Notes

1. When an appreciable quantity of iron is present, sufficient HF must be added not only to complex this element (thus decolorizing the solution) but also to precipitate lanthanum carrier.

2. When the plutonium sample is from underground nuclear debris and is to be subjected to mass spectrometric analysis as well as the regular procedure, aluminum must be removed before *Step 2* of the procedure is performed.

Add the recommended amount of lanthanum carrier, and then add several drops of thymolphthalein indicator solution to the sample, which is 3M in HCl. Place the sample in an ice bath and add enough 50% NaOH to turn the indicator blue. Stir, centrifuge, and discard the supernate. Wash the precipitate with a small amount of H<sub>2</sub>O, stir, centrifuge, and discard the supernate. Dissolve the precipitate in 1 to 2 drops of conc HCl and dilute to 2 to 3 ml with 3M HCl. Continue with *Step 2* of the procedure, but omit the addition of lanthanum carrier.

3. The presence of conc HNO<sub>3</sub> in Solution I is necessary to destroy the reducing properties of the original resin and thus avoid premature reduction of plutonium(IV) to the tripositive state.

4. To fission-count the plutonium, plates may be prepared by taking the activity directly from the column. However, if any drops are permitted to run together (producing an extreme "bathtub effect"), the fission-counting results are invariably too low. To avoid such effects that are attributable to sample thickness, the samples should be electroplated as described in the procedure for ELECTRODEPOSITION OF PLUTONIUM FOR FISSION COUNTING.

5. The neptunium activity that remains on the column after elution of plutonium may be removed in the following manner:

(a) Use pressure to force concentrated HCl that contains several drops of HNO<sub>3</sub>/ml through the column until the dark color has been removed. Discard the effluent. (During this process the column may separate as a result of bubbling, etc., but can be resettled by applying pressure.)

(b) Wash the resin with conc HCl and pressure; permit the column to rebed itself.

(c) Elute the neptunium with 0.1M HCl. The yield may be very low after only one elution with 0.1M HCl; use about three cycles of elution alternately with 0.1M HCl and conc HCl to produce yields up to 85%.

(October 1989)



# ELECTRODEPOSITION OF PLUTONIUM FOR FISSION COUNTING

D. C. Hoffman

## 1. Reagents

HCl: conc; 1M  
HNO<sub>3</sub>: conc  
NH<sub>4</sub>OH: conc  
Ethanol: absolute  
NH<sub>4</sub>Cl: solid  
Methyl red indicator solution

## 2. Procedure

*Step 1.* In a graduated centrifuge tube, collect the eluate from *Step 9* of the PLUTONIUM procedure. (Collect the same amount of eluate that would normally be collected on the platinum disk for pulse analysis). To the eluate add 2 to 3 drops of conc HNO<sub>3</sub> and place the tube in an oil bath that is maintained at ~100°C. Use an air jet to evaporate the solution to dryness. Add 3 drops of conc HCl and take the resulting solution to dryness. Repeat the HCl treatment four times.

*Step 2.* After the final evaporation, take the residue up in 0.5 ml of conc HCl and transfer to an electroplating cell that is equipped with a 1-in. platinum plating disk, a thin-walled chimney, and a plastic gasket (Note). Wash the centrifuge tube with two 0.5-ml portions of distilled H<sub>2</sub>O, and transfer the washings to the plating cell (~1.5-ml volume). Add two small spatulas of NH<sub>4</sub>Cl and 2 drops of methyl red indicator solution. Make the solution alkaline with conc NH<sub>4</sub>OH and then add 1M HCl dropwise until the solution is barely acidic.

*Step 3.* Electroplate at 2 A and ~6.8 V for 15 min while stirring the solution with a graphite rod. Just before plating is completed, add 0.5 ml of conc NH<sub>4</sub>OH. Immediately turn off the stirrer and the current and pour the plating liquid back into the centrifuge tube. Remove the chimney and wash the platinum disk with H<sub>2</sub>O and then with ethanol. Flame the plate and count for 1 min on an alpha counter.

*Step 4.* Use Duco cement to mount the platinum plate on a standard fission mount.

## Note

The electroplating setup is the same as that used in the (Plutonium) URANIUM-235 I procedure.

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# REMOVAL OF $^{239}\text{Pu}$ FROM LANTHANIDES, CESIUM, AND ZIRCONIUM

B. E. Cushing

## 1. Introduction

Plutonium(IV) can be quantitatively removed from the lanthanides, cesium, and zirconium by extraction with triisooctylamine. The separation is not satisfactory if the plutonium is in any other oxidation state than +4. The extraction is carried out in the presence of the appropriate carrier or carriers; for example, if the solution, after removal of plutonium, is to be used for analysis of zirconium, this element is employed as carrier.

## 2. Reagents

Lanthanum carrier: 10 mg lanthanum/ml, added as  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in  $\text{H}_2\text{O}$

Cesium carrier: 10 mg cesium/ml, added as  $\text{CsCl}$  in  $\text{H}_2\text{O}$

Zirconium carrier: 10 mg zirconium/ml, added as  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 1M  $\text{HNO}_3$

$\text{HCl}$ : 5M; conc

$\text{H}_2\text{SO}_4$ : conc

$\text{NaNO}_2$ : 0.1M

Triisooctylamine: 20% by volume in *n*-heptane

## 3. Procedure

All operations are performed in a glove box.

*Step 1.* Pipette an aliquot of the sample into a 50-ml erlenmeyer flask and add 1 ml each of the desired carriers. Add 10 to 20 drops of conc  $\text{H}_2\text{SO}_4$  and heat to fumes of  $\text{SO}_3$ .

*Step 2.* Cool the solution and transfer to a 40-ml glass centrifuge tube with 5 to 10 ml of 5M  $\text{HCl}$ . Add ~10 drops of 0.1M  $\text{NaNO}_2$  and heat in a boiling water bath for 5 min.

*Step 3.* Transfer the solution to a 125-ml separatory funnel and rinse the centrifuge tube with

a minimum amount of 5M  $\text{HCl}$ ; add the rinsings to the separatory funnel. Add an equal volume of 20% (by volume) triisooctylamine in *n*-heptane and shake well.

*Step 4.* Allow the phases to separate and draw off the aqueous phase into a clean 40-ml centrifuge tube.

*Step 5.* To the aqueous extract add 10 drops of 0.1M  $\text{NaNO}_2$  and heat in a boiling water bath for 5 min.

*Step 6.* Repeat *Step 3* (Notes 1 and 2).

## Notes

1. The extraction is repeated if necessary. In one experiment, three extractions were sufficient to completely remove 47 mg of plutonium.

2. This procedure does not remove  $^{241}\text{Am}$  activity. Americium activity may be separated from the plutonium-free aqueous solution by following the additional steps below.

(a) Use ammonia gas to precipitate hydroxides. Centrifuge, discard the supernate, and wash the precipitate with  $\text{H}_2\text{O}$ . Centrifuge and discard the supernate.

(b) Dissolve the precipitate in 1 to 2 drops of conc  $\text{HCl}$  and add 1 ml of 5M  $\text{NH}_4\text{CNS}$  buffered at pH 1.2. Put the solution on an AG 1-X8 anion-exchange resin column (100 to 200 mesh; 1 cm by 6 cm), which has been equilibrated with 5M  $\text{NH}_4\text{CNS}$  solution.

(c) Elute with 10 ml of the cold 5M  $\text{NH}_4\text{CNS}$  solution. This procedure gives a decontamination factor of  $\sim 5 \times 10^3$  and should be repeated to ensure removal of americium.

(October 1989)

# HDEHP SEPARATION OF PLUTONIUM FROM UNDER- GROUND NUCLEAR DEBRIS

D. C. Hoffman and F. O. Lawrence

## 1. Introduction

In this procedure, plutonium is extracted quantitatively into HDEHP (di-2-ethylhexyl phosphoric acid) in *n*-heptane from 4M HNO<sub>3</sub> solutions of the fluoride-soluble fractions obtained from underground nuclear debris. The method is convenient for isolating plutonium from large volumes of solutions of high ionic strength—solutions for which the element does not carry well on a fluoride precipitate. The plutonium is predominantly in the (VI) oxidation state in the samples. The element is recovered from the organic phase by reduction to the (III) state and back-extraction with NH<sub>4</sub>I-HCl solution. This step accomplishes extensive decontamination because most of the species that extract into HDEHP from 4M HNO<sub>3</sub> are not back-extracted by the NH<sub>4</sub>I-HCl solution. Further purification of the plutonium can be accomplished by the usual LaF<sub>3</sub> precipitations and elution from an anion-exchange resin column with HI-HCl solution, as described in the PLUTONIUM procedure.

Plutonium(IV) is also extracted quantitatively by HDEHP in *n*-heptane, but it appears that in this oxidation state the element is so tightly held in the organic phase that it is not effectively reduced and back-extracted.

## 2. Reagents

HDEHP solution: 0.5M solution of di-2-ethylhexyl orthophosphoric acid in *n*-heptane (43 ml—or ~40.25 g—of the acid in 250 ml of solution).

HCl: 9M

HNO<sub>3</sub>: 4M; conc

NH<sub>4</sub>I: saturated aqueous solution

NH<sub>4</sub>I-HCl solution: one volume of the saturated

NH<sub>4</sub>I solution to 8 of 9M HCl

NH<sub>2</sub>OH•HCl: solid

## 3. Procedure

*Step 1.* Pre-equilibrate the 0.5M HDEHP with an equal volume of 4M HNO<sub>3</sub>. To an aliquot of the sample (~4M in HNO<sub>3</sub>) in either a narrow-necked 40-ml conical centrifuge tube or a 60-ml separatory funnel, add one-half to one-third its volume of the pre-equilibrated HDEHP. Shake for 1 min and allow the phases to separate; centrifuge if necessary. Remove the aqueous (bottom) layer and discard. Wash the organic layer by shaking for 1 min with an equal volume of 4M HNO<sub>3</sub>, and discard the wash.

*Step 2.* To the organic phase, add ~50 mg of solid NH<sub>2</sub>OH•HCl and then one-half volume of NH<sub>4</sub>I-HCl solution. Shake for 2 min and drain the aqueous (bottom) layer into a clean 40-ml centrifuge tube. Discard the organic layer.

*Step 3.* If the final volume of the aqueous layer is <10 ml, dilute with H<sub>2</sub>O to about three times the volume and proceed to *Step 2* of the PLUTONIUM procedure. If the volume is >10 ml, transfer the solution to a 125-ml erlenmeyer flask and evaporate to the desired volume over a burner. Then proceed to *Step 2* of the PLUTONIUM procedure. Be sure to oxidize the plutonium(III) by adding 1 drop of conc HNO<sub>3</sub> to the HCl solution and warming just before passing it through the anion resin column.

(October 1989)

# THE SEPARATION OF PLUTONIUM FROM LARGE VOLUMES OF SOLUTION I

D. C. Hoffman and F. O. Lawrence

## 1. Introduction

The basic principle in the separation of plutonium from large volumes of solution is the same as that used in the procedure for HDEHP SEPARATION OF PLUTONIUM FROM UNDERGROUND NUCLEAR DEBRIS, in which plutonium is extracted quantitatively into HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane from acidic solution. In the procedure described below, the plutonium is extracted into HDEHP-*n*-heptane that has been impregnated on an inert support (a fluorohalocarbon resin). Extraction on such a column is much more convenient than one in which the plutonium-containing solution is extracted with a large volume of HDEHP solution. Moreover, the back-extraction of plutonium from the column is more efficient than from HDEHP solution. With the use of the column, the separation of phases is clean—which is not always true in ordinary liquid-liquid extraction.

## 2. Reagents

$^{236}\text{Pu}$  standardized tracer solution, in 3*M* HCl  
HCl: 9*M*; 4*M*  
 $\text{CrO}_3$ : solid  
 $\text{NH}_4\text{I}$ : saturated aqueous solution  
 $\text{NH}_4\text{I-HCl}$ : one volume of saturated  $\text{NH}_4\text{I}$  solution  
to eight volumes of 9*M* HCl  
 $\text{NH}_2\text{OH}\cdot\text{HCl}$ : solid  
CTFE-2300 (fluorohalocarbon resin) powder:  
source: Allied Chemical Corporation,  
Morristown, New Jersey  
HDEHP: di-2-ethylhexyl orthophosphoric acid:  
purified according to the directions in the  
Reference.  
*n*-heptane

## 3. Procedure

*Step 1.* Pipette the tracer plutonium and the sample in 4*M* HCl into an erlenmeyer flask and add a few crystals of  $\text{CrO}_3$ . Heat to boiling and then let cool to room temperature.

*Step 2.* To the CTFE-2300 (1 g/50 ml of sample solution) (Note), add enough of a mixture of equal volumes of purified HDEHP and *n*-heptane to make a slurry. Allow to equilibrate for 5 min. Stir well; pour the resulting mixture into a glass column (i.d. ~1 cm), the tip of which has been plugged with glass wool. Wash the column with 2 ml of 4*M* HCl.

*Step 3.* Pour the cooled, sample-containing mixture onto the column and allow it to pass through either under gravity or with the application of a slight air pressure. Discard the effluent.

*Step 4.* Wash the (resin) column with 2 ml of 4*M* HCl and then with 2 ml of 9*M* HCl. Discard the washings. Add a few crystals of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  to the top of the column.

*Step 5.* Add 2 ml of  $\text{NH}_4\text{I-HCl}$  solution to the column to elute the plutonium, and collect the eluate in a 40-ml glass centrifuge tube.

*Step 6.* Dilute the eluate to 3*M* in HCl by addition of the appropriate quantity of  $\text{H}_2\text{O}$ . Perform *Steps 2* through *10* of the PLUTONIUM procedure.

## Note

Different batches of CTFE vary somewhat in their properties, so different support-to-sample ratios may be necessary.

## Reference

K. Wolfsberg, Ph.D. Thesis, Washington University, St. Louis, Missouri (1959), p. 60.

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# THE SEPARATION OF PLUTONIUM FROM LARGE VOLUMES OF SOLUTION II

F. O. Lawrence and D. C. Hoffman

## 1. Introduction

In this procedure, DBHQ, (2,5-di-tertiary butylhydroquinone) in 2-ethyl-1-hexanol solution is used for the back-extraction of plutonium(IV) from solutions of HDEHP (di-2-ethylhexyl orthophosphoric acid) in *n*-heptane.

Treatment with DBHQ reagent, followed by contact with 6M HCl, will back-extract both plutonium(IV) and (VI) quantitatively from HDEHP-*n*-heptane solutions. Plutonium(IV), once extracted into HDEHP solutions, is apparently so tightly complexed that previous attempts to back-extract it quantitatively with other reagents, even with those which should reduce the element to the tripositive state, have been unsuccessful. Presumably, in the back-extraction with the DBHQ solution, the plutonium is reduced to the +3 state and then strongly complexed by the DBHQ.

The extraction coefficients (for transfer from aqueous media to HDEHP solution) for plutonium(IV) are very much higher than for plutonium(VI). The volume of HDEHP extractant for the former species can be as little as one-fifth the volume of the sample. The procedure can be adapted readily to a mixture of the two plutonium species by increasing the volume of HDEHP extractant to one-third of the sample volume.

To determine the element quantitatively,  $^{236}\text{Pu}$  tracer is added;  $\text{NaNO}_2$  is used to ensure that all the plutonium is converted to the +4 state to effect complete exchange.

## 2. Reagents

$^{236}\text{Pu}$  standardized tracer solution in 3M HCl  
HDEHP solution: 0.75M solution of di-2-ethylhexyl orthophosphoric acid in *n*-heptane  
DBHQ solution: 0.2M solution of 2,5-di-tertiary butylhydroquinone in 2-ethyl-1-hexanol  
HCl: 6M; 3M  
 $\text{NaNO}_2$ : 10M

## 3. Procedure

*Step 1.* Pre-equilibrate the 0.75M HDEHP solution with an equal volume of 3M HCl in a separatory funnel. (The size of the funnel should be about twice that of the sample aliquot.) Add sufficient 10M  $\text{NaNO}_2$  to an aliquot of the sample and the plutonium tracer (in either a narrow-necked conical centrifuge tube or an erlenmeyer flask) to make the final concentration of the salt  $\sim 0.2M$ ; for example, add 1 ml of 10M  $\text{NaNO}_2$  to 50 ml of aliquot of sample. Heat the solution to boiling and then permit it to cool to room temperature. Add the sample to one-third its volume of pre-equilibrated HDEHP, shake for 1 min, and allow the two phases to separate; centrifuge if necessary (Note). Remove the aqueous (bottom) layer and discard. Wash the organic layer by shaking for 1 min with an equal volume of 6M HCl, and discard the wash.

*Step 2.* To the organic phase add one-third volume of the 0.2M DBHQ solution and shake for  $\sim 10$  s. Add one-half volume of 6M HCl, shake for  $\sim 2$  min, and allow 5 min for the separation of the two phases. Drain, save the aqueous (lower) phase, and discard the organic layer.

*Step 3.* If the volume of the aqueous phase is  $< 5$  ml, add  $\text{H}_2\text{O}$  to make the solution 3M in acid and proceed to *Step 2* of the PLUTONIUM procedure. If the volume of the aqueous phase is  $> 5$  ml, transfer the solution to a 125-ml

erlenmeyer flask and evaporate over a burner. Transfer the solution to a 40-ml conical centrifuge tube, use water washes from the erlenmeyer flask to dilute the solution to 3M in acid, and then continue with *Step 2* of the PLUTONIUM procedure.

#### Note

If very large aliquots (150 to 200 ml) of sample are used, the volume of HDEHP solution may be increased to one-half volume of that of the sample and a second back-extraction with 6M HCl may be performed.

#### Addendum

If large amounts of thorium are present, complete the above procedure and carry out *Steps 2* through *4* of the regular PLUTONIUM procedure. Then dissolve the LaF<sub>3</sub> by stirring with 2 to 3 drops of saturated H<sub>3</sub>BO<sub>3</sub> solution. Add 3 ml of 10M HCl and transfer the solution to a 6-cm by 4-mm Bio-Rad AG 50W-X4, minus 400 mesh, cation resin (H<sup>+</sup> form) column. (Before using, wash the column with 10M HCl.) Collect the effluent in a 125-ml erlenmeyer flask. Wash the column once with 3 ml of 10M HCl and twice with 6 ml of conc HCl; collect the effluents in the erlenmeyer flask. Boil down the combined effluents to a small volume (0.5 to 2 ml) and transfer the solution to a 40-ml glass centrifuge tube. Dilute with sufficient H<sub>2</sub>O to make the solution 3M in HCl and proceed with *Step 2* of the PLUTONIUM procedure.

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# SEPARATION OF URANIUM AND PLUTONIUM FROM UNDER- GROUND NUCLEAR DEBRIS FOR MASS SPECTROMETRIC ANALYSIS

G. W. Knobeloch, V. M. Armijo,  
and D. W. Eford

## 1. Introduction

The major steps in this procedure for the separation of uranium and plutonium include: (1) exchange of uranium in the sample with  $^{233}\text{U}$  and of plutonium with  $^{242}\text{Pu}$ ; (2) extraction of these elements as nitrates into ethyl acetate from a 1M  $\text{HNO}_3$  solution saturated with  $\text{NH}_4\text{NO}_3$ ; (3) back-extraction into  $\text{H}_2\text{O}$ ; (4) adsorption of the uranium and plutonium on an anion-exchange resin column; (5) washes with 0.1M  $\text{H}_2\text{SO}_4$  and 10M  $\text{HCl}$ , followed by elution of plutonium(III) by means of an  $\text{HI-HCl}$  mixture and uranium by  $\text{HNO}_3$  after washes with 0.1M  $\text{H}_2\text{SO}_4$  and 8M  $\text{HCl}$ ; and (6) separate treatment of the uranium and plutonium on macroporous anion-exchange resins; the elements are adsorbed from a  $\text{H}_2\text{O}_2\text{-HCl}$  solution, and after appropriate washes of the resins, the uranium is eluted with  $\text{H}_2\text{O}$  and the plutonium with  $\text{HBr}$ .

The extraction and back-extraction processes are quite effective in removing fission products and the elements present in macro amounts in soil samples (for example, sodium, potassium, magnesium, calcium, aluminum, silicon, and iron). After the back-extraction, the plutonium, about half of the neptunium, some  $^{95}\text{Zr}$  and  $^{97}\text{Zr}$ ,  $^{95}\text{Nb}$ ,  $^{99}\text{Tc}$ ,  $^{103}\text{Ru}$ ,  $^{229}\text{Th}$ ,  $^{131}\text{Te}$ , and  $^{132}\text{Te}$  remain with the uranium. Relatively large amounts of the salting out agent,  $\text{NH}_4\text{NO}_3$ , are also present and carry along enough of the alkali metals and iron to interfere with mass spectrometric analysis. The main purpose of the anion resin column step is the removal of these interferences. Last traces of iron are removed by the  $\text{H}_2\text{SO}_4$  wash. Large amounts of  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  used in washing the resin, relative to the free column volume, are necessary to remove all traces of

the alkali metals. At the completion of the column step, gamma-spectral analysis reveals that the major contaminant is zirconium and that only a little  $^{99}\text{Tc}$  and  $^{95}\text{Nb}$  are present. Emission-spectral analysis shows less than 1 ppm of sodium, potassium, calcium, aluminum, and iron in both the plutonium and uranium; there is also some uranium contaminant in the plutonium and some thorium and plutonium contaminant in the uranium. The macroporous anion-exchange resin column treatments are necessary to achieve additional levels of purity required for pulse-counting mass spectroscopy. Uranium recovery is ~80% and plutonium recovery ~75%.

The procedure has been used for samples containing as little as 5 ng of uranium and plutonium. A "clean" laboratory and the purest available reagents are required.

## 2. Reagents

$^{233}\text{U}$  tracer: source, National Bureau of Standards (NBS)

$^{242}\text{Pu}$  tracer

$\text{HClO}_4$ : conc

$\text{HNO}_3$ : conc; 8M; 2M; 1M

$\text{HBr}$ : 47%; source, MCB Reagents

$\text{HCl}$ : 10M; 8M; 6M; 1.5M

$\text{H}_2\text{SO}_4$ : 0.1M

Aqua regia: 3:1 mixture, by volume, of 10M  $\text{HCl}$  and conc  $\text{HNO}_3$

$\text{HI-HCl}$  mixture: 1:9 mixture, by volume, of 48%  $\text{HI}$  and 10M  $\text{HCl}$

$\text{H}_2\text{O}$ : Type 1 reagent-grade water (deionized)

$\text{H}_2\text{O}_2\text{-HCl}$  reagent: 1 drop of 30%  $\text{H}_2\text{O}_2$  to 9 ml of 10M  $\text{HCl}$

$\text{NH}_4\text{NO}_3$ : solid

Ethyl acetate

Bio-Rad macroporous anion-exchange resin: AGMP-1, 50 to 100 mesh, granular, deionized water slurry. This resin is pretreated by warming overnight in a mixture of 50% 10M  $\text{HCl}$  and 50%  $\text{H}_2\text{O}$ . It is washed 20 times with deionized  $\text{H}_2\text{O}$  and stored as an  $\text{H}_2\text{O}$  slurry. The column uses a disposable automatic

pipette tip, ~7 cm long and 5 mm i.d. A plug of prewashed quartz wool is placed in the tip and resin is added to a depth of ~2 cm.

### 3. Procedure

*Step 1.* Place an aliquot of sample (Note 1) containing 100 to 200 ng of uranium in 3M HCl in a 40-ml centrifuge tube. Add  $^{233}\text{U}$  tracer in amount to provide approximately equivalent ratios of  $^{233}/^{235}$  and  $^{238}/^{233}$ , and then add  $^{242}\text{Pu}$  tracer equal to the estimated quantity of  $^{239}\text{Pu}$ . Add 2 ml of conc  $\text{HClO}_4$  and evaporate to dryness (Note 2).

*Step 2.* Add 5 ml of 2M  $\text{HNO}_3$  and sufficient solid  $\text{NH}_4\text{NO}_3$  to saturate the solution, and warm to room temperature. (The addition of the  $\text{NH}_4\text{NO}_3$  approximately doubles the volume of solution). Add 10 ml of ethyl acetate, stopper the tube with a plastic top, and shake for 1 min. Centrifuge lightly to separate the phases, remove the ethyl acetate (top) layer, and transfer it to a clean centrifuge tube. Repeat the extraction twice and combine the ethyl acetate phases. Discard the aqueous phase.

*Step 3.* Wash the combined ethyl acetate phases with 3 ml of 2M  $\text{HNO}_3$  that has been saturated with  $\text{NH}_4\text{NO}_3$  and equilibrated against ethyl acetate. Centrifuge and discard the wash. Wash twice more, discarding the washes. (The washes remove aqueous entrainments in the ethyl acetate.) Back-extract uranium and plutonium with 10 ml of  $\text{H}_2\text{O}$ , centrifuge, and transfer the aqueous layer to a clean centrifuge tube. Repeat the back-extraction twice more, combining the aqueous layers. Discard the ethyl acetate layer (Note 3).

*Step 4.* Evaporate the aqueous layer to dryness in a heating block. Wash down the walls of the tube with 1 ml of aqua regia and heat to dryness to destroy  $\text{NH}_4\text{NO}_3$ . Add 1 ml of 10M HCl and evaporate to dryness. Add 1 ml of 0.1M  $\text{H}_2\text{SO}_4$ , warm (Note 4), and place the solution on a Bio-Rad AGMP-1, 50 to 100 mesh, anion-exchange resin column that has previously been subjected to three

1-ml  $\text{H}_2\text{O}$  washes and one 1-ml 0.1M  $\text{H}_2\text{SO}_4$  wash. Discard the effluent. Wash the tube with 1 ml of 0.1M  $\text{H}_2\text{SO}_4$  and add the wash to the resin column (Note 5). Discard the effluent. Add 1 ml of 10M HCl containing a trace of  $\text{HNO}_3$  (10 ml of HCl + 1 drop of conc  $\text{HNO}_3$ ) to the column and discard the effluent. Rinse the tip of the column with a stream of deionized  $\text{H}_2\text{O}$ .

*Step 5.* To remove the plutonium remaining on the column, use three successive additions of 9 drops of HI-HCl mixture to reduce that element to the +3 state; collect the eluate that contains plutonium in a 40-ml centrifuge tube. Wash the column with 1 ml of 8M HCl. Wash the tip of the column with a stream of deionized  $\text{H}_2\text{O}$ .

*Step 6.* Elute uranium with 1 ml of 1M  $\text{HNO}_3$  and 1 ml of conc  $\text{HNO}_3$  and collect the eluate in a 40-ml centrifugal tube.

*Step 7.* The uranium and plutonium samples at this point are not free enough of impurities to permit mass spectrometric analysis by the pulse-counting technique. Each fraction is evaporated to dryness in its centrifuge tube on a heating block. To destroy residual  $\text{I}^-$ , add 1 drop of conc  $\text{HNO}_3$  to the plutonium and evaporate the solution to dryness again. Repeat the evaporation, using 1 drop of 10M HCl. Add 1 ml of the  $\text{H}_2\text{O}_2$ -HCl reagent to dissolve each sample.

*The Uranium Sample:* Place the solution onto a Bio-Rad macroporous AGMP-1, 50 to 100 mesh, anion-exchange resin column that has been subjected to two 1-ml  $\text{H}_2\text{O}$  washes and three 1-ml  $\text{H}_2\text{O}_2$ -HCl reagent washes. Use one additional portion of 1 ml of the  $\text{H}_2\text{O}_2$ -HCl reagent to rinse the centrifuge tube and pass the rinsing through the column. Discard both effluents. Wash the zirconium off the column with 15 drops of 6M HCl. Wash the tip of the column with a stream of deionized  $\text{H}_2\text{O}$  and elute the uranium with three successive 1-ml portions of deionized  $\text{H}_2\text{O}$ ; collect the eluates in a 40-ml centrifuge tube (Note 6). Transfer enough of the uranium solution



to supply 50 ng of the element to a quartz test tube. Evaporate the solution to dryness in a heating block. Add 3 drops of conc  $\text{HNO}_3$  and 3 drops of conc  $\text{HClO}_4$  and heat to  $130^\circ\text{C}$  for 1 h. Evaporate to dryness at a temperature  $>180^\circ\text{C}$ . Cool and cap the quartz tube. The sample is ready for mass spectrometric analysis.

*The Plutonium Sample:* The plutonium fraction still contains too much zirconium to permit mass spectrometric analysis and enough  $^{238}\text{U}$  to affect the determination of  $^{238}\text{U}$ . For purification, pass the  $\text{H}_2\text{O}_2$ - $\text{HCl}$  solution through a macroporous anion-exchange resin column like that used for uranium. Pass 1 ml of  $\text{H}_2\text{O}_2$ - $\text{HCl}$  reagent through the column and wash off the uranium and zirconium with 60 drops of 8M  $\text{HNO}_3$  (Note 7). Wash the tip of the column with a stream of deionized  $\text{H}_2\text{O}$  and elute the plutonium with three 1-ml portions of 47%  $\text{HBr}$  into a quartz test tube. At this point, an aliquot is removed for alpha assay to ascertain the amount of plutonium that will be supplied for mass spectrometric analysis.

Evaporate the  $\text{HBr}$  solution of plutonium to dryness in a heating block. Destroy the traces of  $\text{HBr}$  and organic material from the remaining macroporous anion resin by adding 3 drops of conc  $\text{HNO}_3$  and 3 drops of conc  $\text{HClO}_4$  and heating to  $130^\circ\text{C}$  for 1 h in a heating block. Evaporate to dryness at a temperature greater than  $180^\circ\text{C}$ . Cool and cap the quartz tube. The sample is ready for mass spectrometric analysis.

## Notes

1. The usual size of sample is 10 to 100 mg. If more than 0.33 g of soil is required to meet plutonium requirements, it is suggested that fluoride precipitation, dissolution of the precipitate in  $\text{HCl} + \text{H}_3\text{BO}_3$  solution, and boiling with 9M  $\text{NaOH}$  be carried out as preliminary steps, after Step 1 has been performed.

2. It is essential to achieve exchange between the tracers and sample atoms. This is accomplished

by allowing the sample plus tracer to evaporate to dryness overnight in a heating block (at  $\sim 110^\circ\text{C}$ ) followed by at least one strong fuming ( $\text{HClO}_4$ ) period over a burner.

3. At this point, the macro soil constituents, sodium, potassium, magnesium, calcium, aluminum, and iron, and most fission products have been removed. The remaining elements are:  $\sim 95\%$  of the uranium,  $\sim 80\%$  of the plutonium,  $\sim 50\%$  of the neptunium, 60 to 80% of the zirconium, and traces of niobium, technetium, ruthenium, tellurium, and iron; of course,  $\text{NH}_4\text{NO}_3$  also remains.

4. When dealing with nanogram quantities of uranium and plutonium, it is advisable to be thorough and patient in dissolving their nitrates from a dry state. Flaming the tubes to dryness should be avoided because the baked oxides formed will stick to the glass and be difficult to remove. Check for removal of  $^{237}\text{U}$  with a radiation meter, if possible.

5. The  $\text{H}_2\text{SO}_4$  is effective in the removal of the remaining  $^{239}\text{Np}$  and the last traces of iron that would interfere with the mass spectrometric measurement. Approximately 5% of the plutonium is washed off with the 0.1M  $\text{H}_2\text{SO}_4$ , but uranium sticks quantitatively. In Step 4 when the uranium and plutonium are being dissolved in the warm 0.1M  $\text{H}_2\text{SO}_4$ , care must be taken to avoid concentration of the  $\text{H}_2\text{SO}_4$  by evaporation. A 0.5M  $\text{H}_2\text{SO}_4$  can remove 100% of the plutonium and 50% of the uranium. It is necessary to record the time here as the time of separation of plutonium and neptunium. This is also a convenient record of the separation of plutonium and curium, which is achieved here and in the extraction. This permits corrections to the  $^{238}\text{Pu}$  mass peak.

6. The final solution is assayed for  $^{233}\text{U}$  by alpha-counting to determine chemical yield. Also, at this point an aliquot may be removed for  $^{237}\text{U}$  measurement by beta- or gamma-counting.

7. Variations in the uranium, plutonium, zirconium, etc., ratios in the starting samples, as well as slight variances in column preparation, will result in slight differences in the amounts of 8M HNO<sub>3</sub> needed here and in the quantities of 6M HCl required on the macroporous anion resin cleanup column. Therefore, the relative amount of <sup>95</sup>Zr (by means of its 724- and 756-keV gammas) and of <sup>237</sup>U (by means of its 208-keV gamma) should be ascertained with a multichannel pulse height analyzer and the amount of <sup>239</sup>Pu should be determined by alpha-counting. With such information the quantities of column washes may be adjusted to obtain the best level of decontamination.

(October 1989)

## APPENDIX E

# PREPARATION OF PLUTONIUM SAMPLES FOR MASS SPECTROMETRIC ANALYSIS

# PREPARATION OF PLUTONIUM SAMPLES FOR MASS SPECTROMETRIC ANALYSIS

R. E. Perrin and H. L. Smith

## 1. Introduction

To prepare plutonium samples for mass spectrometric analysis, the basic PLUTONIUM procedure is first carried out. After the element has been counted (*Step 10* of that procedure), it is removed from the platinum disk by repeated treatment with HF and HCl. The acidic solution is fumed to dryness with conc HNO<sub>3</sub> and HClO<sub>4</sub>, and the residue is dissolved in 9M HCl that contains enough H<sub>2</sub>O<sub>2</sub> to keep plutonium in the +6 oxidation state. The plutonium is then placed on a macroporous anion-exchange resin; uranium and iron are also adsorbed. The plutonium is removed from the column by elution with conc HBr; the uranium and iron stay on the column.

## 2. Reagents

HF: 2.7M

HCl: 3M; obtained by diluting National Bureau of Standards (NBS) sub-boiling distilled reagent

9M HCl: The reagent is used to pick up the sample after the HClO<sub>4</sub> fuming step and to rinse the column free of americium. The reagent is prepared by sub-boiling distillation or is purchased from NBS. Just before use, 10 ml of acid containing 1 drop of 30% H<sub>2</sub>O<sub>2</sub> is warmed at ~90°C for 20 to 30 min to ensure the presence of a small amount of free Cl<sub>2</sub>, which prevents reduction of plutonium on the column.

HNO<sub>3</sub>: conc; source: NBS

HClO<sub>4</sub>: conc; source: NBS

8.8M HBr: E. M. 306-7S Suprapur: source:  
E. Merck, Darmstadt, West Germany

Anion-exchange resin: Bio-Rad AGMP-1, 50 to  
100 mesh

H<sub>2</sub>O: Use only H<sub>2</sub>O that has been deionized by  
passing through a Milli-Q H<sub>2</sub>O system.

## 3. Ion-Exchange Column Preparation

Disposable plastic pipette tips are used for ion-exchange columns. These are cleaned by immersion in 8M HNO<sub>3</sub> at 80°C for 48 h. The tips are then rinsed thoroughly with Milli-Q H<sub>2</sub>O and dried by two rinses in glass-distilled acetone. After air-drying in a class 100 clean-air hood, the tips are sealed in batches of 10 in plastic bags for storage.

Quartz wool is cleaned by immersion in 8M HNO<sub>3</sub> at ~80°C for 48 h. After thorough rinsing in Milli-Q H<sub>2</sub>O, the wool is air-dried under a heat lamp in a 100 plus hood. Small portions of the quartz wool are stored in 15-ml plastic vials that have been cleaned in a like manner.

Bio-Rad AGMP-1 resin, 50 to 100 mesh, is prepared by being washed thoroughly in 9M HCl three times. After the resin has settled, the excess HCl is poured off, and the resin is stored under fresh 9M HCl in 30-ml plastic bottles cleaned with 8M HNO<sub>3</sub> (as previously described for the disposable pipette tips).

All transfers are performed using transfer pipettes, which are cleaned by immersion in 8M HNO<sub>3</sub> for 48 h at 80°C. After thorough rinsing with Milli-Q H<sub>2</sub>O, the pipettes are air-dried in a 100 plus hood. The cleaned pipettes are stored in sealed plastic bags in batches of five.

All separations are performed using 13- by 100-mm Pyrex or quartz tubes that have been cleaned by immersion in 8M HNO<sub>3</sub> for 48 h at 80°C. After thorough rinsing with Milli-Q H<sub>2</sub>O, the tubes are air-dried (open end down) in a 100 plus hood. The tubes are then sealed in batches of two in plastic for future use. Pyrex tubes are used for column preparation and americium elution. Quartz tubes are used for the final elution step and boil down.

Prepare the ion-exchange column as follows.

1. Place a small quartz wool plug in the end of a clean plastic pipette tip. The plug should be ~2 mm long. A clean transfer pipette tip works well for tamping the plug into the pipette tip.

2. Place a plastic collar over the ion-exchange column. This collar is made by cutting the end of a 3X tapered stopper with a razor blade. A small V is cut in the base of the stopper (see Fig. 1) to prevent formation of an air lock.

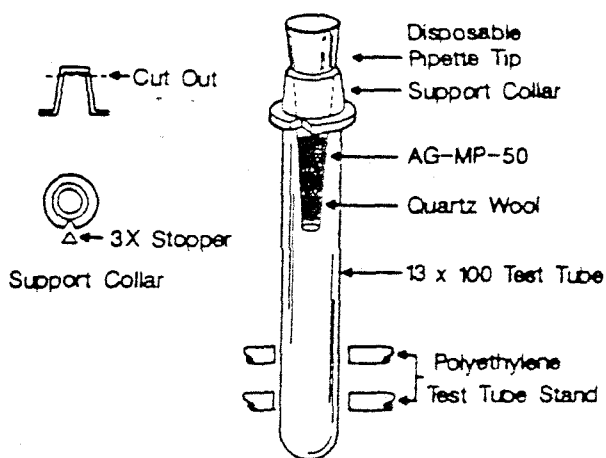


Fig. 1. Details of micro ion-exchange column.

3. Place the pipette tip with collar in a clean 13- by 100-mm Pyrex test tube supported in a plastic test tube rack.

4. Using a clean transfer pipette, transfer enough AGMP-1 resin to form a resin column 1 cm long in the pipette tip.

5. Rinse the resin column with 3 column volumes of 9M HCl containing a trace of free  $\text{Cl}_2$ .

#### 4. Procedure

This procedure assumes that the plutonium sample has been processed through the PLUTONIUM procedure.

*Step 1.* To the platinum disk from *Step 10* of the PLUTONIUM procedure, add sufficient 2.7M HF to cover the spots containing activity. Evaporate the liquid to dryness and add enough 3M (or more conc) HCl to cover the active sites. Warm gently and, by means of a transfer pipette, add the liquid to a Pyrex tube of appropriate size. Repeat the step (both HF and HCl additions) until the desired activity has been removed.

*Step 2.* Add a few drops of conc  $\text{HNO}_3$  and evaporate the solution to a small volume. Then add a few drops of conc  $\text{HClO}_4$  and fume to dryness.

*Step 3.* To the dry Pyrex tube containing the recovered plutonium, add ~1 ml of 9M HCl containing a trace of free  $\text{Cl}_2$ . Warm to ~80°C to ensure dissolution of the plutonium.

*Step 4.* Using a clean transfer pipette, load the solution on an anion-exchange column prepared as previously described. Support the column with a clean 13- by 100-mm Pyrex tube and discard the rinses. (It may be desirable to retain all effluents until the analysis is completed.)

*Step 5.* Using a clean transfer pipette, rinse the column with 5 column volumes of 9M HCl. Allow the fluid level to just reach the resin surface between rinses. This rinse will remove all alkali metals; the last traces of americium, uranium, iron, and plutonium are retained on the column.

*Step 6.* Remove the column from the test tube and thoroughly rinse the tip of the column with 9M HCl to remove the last traces of the impurities.

*Step 7.* Transfer the column to a clean 13- by 100-mm quartz tube. Rinse the column with 5 column volumes of 8.8M HBr. This rinse will elute the plutonium and leave all uranium and iron behind. This step is of particular importance because the presence of iron interferes with subsequent electrodeposition of plutonium.

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*Step 8.* Remove and discard the ion-exchange column. Transfer the quartz tube to a heater block at  $\sim 130^{\circ}\text{C}$  and evaporate the solution to dryness using heat and a stream of filtered air.

*Step 9.* Wash down the sides of the tube with 1.0 to 1.5 ml of Milli-Q  $\text{H}_2\text{O}$  and fume to  $\sim 0.5$  ml. Add 3 to 4 drops of conc  $\text{HNO}_3$  and fume to dryness. Add 3 drops of conc  $\text{HClO}_4$  and evaporate to fumes at  $130^{\circ}\text{C}$ . Increase the temperature to  $180^{\circ}\text{C}$  and fume for 1 h, adding  $\text{HClO}_4$  as necessary. Then fume to dryness to ensure destruction of  $+3$  plutonium polymers and oxidation of any organic matter present. The sample is ready for mass spectrometric analysis. After cooling, cap the test tube with a clean 3X plastic stopper (cleaned by immersion in  $8M$   $\text{HNO}_3$  for 48 h and rinsed with Milli-Q  $\text{H}_2\text{O}$ ). Seal the capped tube in plastic and submit for the mass spectrographic analysis. (The total plutonium submitted should be known to at least 10% to prevent errors in selecting the aliquot size for mass spectrometric analysis.)

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## APPENDIX F

# IN SITU CHEMICAL REMEDIATION OF RADIONUCLIDES IN SOILS

## FY 93/94 SCHEDULES

TECHNICAL TASK PLAN RF 121101  
IN SITU CHEMICAL REMEDIATION OF RADIONUCLIDES IN SOILS  
FY 93 AND FY 94 SCHEDULES

ID	WBS Act	Name	Duration	Start	Finish	93				1994			
						Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2
1	0000	ENTIRE PROJECT SUMMARY	466d	5/1/93	3/15/95								
2	0100	FY 93 PROGRAM SUMMARY	104d	5/5/93	9/30/93								
3		TTP Management Activities	104d	5/5/93	9/30/93								
4	0101	FY 93 TTP PLAN	104d	5/5/93	9/30/93								
5		FY 93 Project Mgmt/tech.coord.	104d	5/5/93	9/30/93								
6		Prepare TTP	19d	5/23/93	6/18/93								
7		Presentation to DOE	1d	6/15/93	6/15/93								
8		EG&G Issue Commitment Letter to DOE	0d	7/21/93	7/21/93								
9		MS-1 DOE Approval	0d	8/2/93	8/2/93								
10		DOE Extension on TTP Funding	0d	8/9/93	8/9/93								
11	0110	PREPARE Workplan	34d	6/21/93	8/9/93								
12		Begin Work Plan Preparation	0d	6/21/93	6/21/93								
13		Workplan Preparation	30d	6/21/93	8/2/93								
20		Complete Workplan	0d	8/2/93	8/2/93								
21	0119	MS (a)- WORK/TEST PLAN ISSUED	0d	8/9/93	8/9/93								
22	0120	FIELD ACTIVITIES	33d	6/28/93	8/13/93								
23	0122	Soil Sampling	29d	6/28/93	8/6/93								
26	0129	MS (b)-Soil Samples Delivered to LANL	0d	8/13/93	8/13/93								
27	0130	BENCH SCALE LAB. ACTIVITIES	51d	7/20/93	9/30/93								
28		Begin Bench Scale experiment designs	0d	7/20/93	7/20/93								
29	0132	Conduct Initial Radioactive Sample Testing	47d	7/26/93	9/29/93								
30		Set up RAD. Experiments LANL	10d	7/26/93	8/6/93								
31		Begin Benchscale Experiments	0d	8/6/93	8/6/93								
32		Perform Analytical Lab. Tests + valid.at LANL	17d	8/6/93	8/30/93								
33		Complete Benchscale Experiments	0d	8/30/93	8/30/93								



# IN SITU CHEMICAL REMEDIATION OF RADIONUCLIDES IN SOILS

## FY 93 AND FY 94 SCHEDULES

ID	WBS Act	Name	Duration	Start	Finish	93				1994			
						Qtr 3	Qtr 4	Qtr 1	Qtr 2	Qtr 3	Qtr 4	Qtr 1	Qtr 2
34		Prepare Bench Scale Letter Report	20d	9/1/93	9/29/93								
35	0139	MS (cl)- Issue Letter Report on Initial Bench Scale Tests	0d	9/30/93	9/30/93								
36	0200	FY 94 PROGRAM SUMMARY	216d	5/1/93	3/15/94								
37	0210	FY 94 Program Management	50d	7/29/93	10/7/93								
38	0211	FY 94 TTP Modifications	22d	8/22/93	9/22/93								
44	0212	LANL/LLNL ICO Contracts for FY 94	50d	7/29/93	10/7/93								
51	0213	FY 94 WORK PACKAGE PREPARATION	24d	8/26/93	9/30/93								
54	0220	CONDUCT BENCH SCALE TESTING PROGRAMS-Second Set Rad. Tests	78d	10/5/93	1/31/94								
55		Begin Second Set Benchscale Experiments	0d	10/5/93	10/5/93								
56		Design Experiments 881 Lab	10d	10/5/93	10/18/93								
57		Conduct . Experiments at 881 Lab	30d	10/13/93	11/23/93								
58		Setup Experiments LANL Lab	10d	10/13/93	10/26/93								
59		Conduct . Experiments at LANL Lab	30d	10/26/93	12/8/93								
60		Perform Analytical Lab. Tests + valid.at LANL/881	30d	12/8/93	1/25/94								
61		Interim Report/Lab Notes Review/Meeting/RFP	5d	1/25/94	1/31/94								
62		MS (dl)- Issue Second Bench Scale Letter Report	0d	1/31/94	1/31/94								
63													
64	0230	SUMMARY 881 Lab Operations	164d	5/1/93	12/23/93								
101	0300	DEVELOP Conceptual Design-Pilot Scale Test Plan	54d	12/5/93	2/24/94								
108	0400	BENCH SCALE SUMMARY REPORTS	30d	2/1/94	3/15/94								
109	0410	Preparation Draft Report-Eg&G	15d	2/1/94	2/21/94								
110	0420	DOE Review and Comments and EDITS	15d	2/7/94	2/25/94								
111	0498	MS (f)- EG&G Issue FINAL Bench Scale Report	0d	3/15/94	3/15/94								
112	0499	MS: FY 94 BENCH SCALE TEST PROGRAM COMPLETE	0d	3/31/94	3/31/94								
113	0500	PILOT SCALE TEST PROGRAM SUMMARY	353d	10/12/93	3/15/95								